TITTABAWASSEE RIVER
AQUATIC ECOLOGICAL RISK ASSESSMENT

POLYCHLORINATED DIBENZO-*P*-DIOXINS
POLYCHLORINATED DIBENZOFURANS

SUBMITTED TO: MICHIGAN DEPARTMENT OF ENVIRONMENTAL QUALITY,
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LIST OF ACRONYMS

ACOE	U.S. Army Corps of Engineers
BMF	Biomagnification Factor
DW	Dry Weight
ERA	Ecological Risk Assessment
FEC	Frank Effect Concentration
GES	Galbraith Environmental Sciences LLC
HI	Hazard Index
HxCDF	Hexachlorodibenzofuran
LD98	Lethal Dose that killed 98% of test organisms
LD50	Lethal Dose that killed 50% of test organisms
LOAEC	Lowest Observed Adverse Effect Concentration
MDEQ	Michigan Department of Environmental Quality
NOAEC	No Observed Adverse Effect Concentration
NWR	National Wildlife Refuge
PCB	Polychlorinated Biphenyl
PCDD	Polychlorinated Dibenzo-*p*-dioxin
PCDF	Polychlorinated Dibenzofuran
PeCDF	Pentachlorodibenzofuran
PCH	Polychlorinated Hydrocarbon
PCOC	Potential Contaminant of Concern
Pg/g	Picograms/gram
STC	Sediment Threshold Concentration
TEF	Toxicity Equivalence Factor
TCDD	Tetrachlorodibenzo-*p*-dioxin
TCDF	Tetrachlorodibenzofuran
TCDD-EQ	TCDD-Equivalent
TRV	Toxicity Reference Value
U.S. EPA	United States Environmental Protection Agency
USFWS	United States Fish and Wildlife Service
WHO	World Health Organization
WW	Wet weight

EXECUTIVE SUMMARY

Risks to birds and mammals from consuming fish from the Tittabawassee River below Midland were evaluated using site-specific contaminant data (fish tissue and bird egg concentrations) and data from the scientific literature. The results of this analysis show that:

- Fish prey of piscivorous (i.e., fish-eating) birds and mammals in the Tittabawassee River below the City of Midland are contaminated with polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs).

- The concentrations of PCDDs and PCDFs in at least four species of fish in the Tittabawassee River (i.e., carp, catfish, shad and smallmouth bass) are sufficiently high as to pose serious risks of reproductive impairment to piscivorous birds and mammals.

- The concentrations of PCDDs and PCDFs in carp, catfish, shad and smallmouth bass exceed levels that are protective of reproductive success in piscivorous birds by factors of up to and exceeding 200.

- The concentrations of PCDDs and PCDFs in carp, catfish, shad and smallmouth bass exceed levels that are protective of reproductive success in piscivorous mammals by factors of up to 60.

- Carp is the most contaminated fish collected from the Tittabawassee River. The concentrations of PCDDs and PCDFs in carp exceed levels that are protective of reproductive success in piscivorous birds by factors of up to over 445.

- The concentrations of PCDDs and PCDFs in carp from the Tittabawassee River exceed levels that are protective of reproductive success in piscivorous mammals by factors of up to 128.

- The concentrations of PCDDs and PCDFs in carp, catfish, shad and smallmouth bass from the Tittabawassee River are sufficiently high to pose risks of reproductive impairment to bird species that are comparatively insensitive, as well as more sensitive species.

- Specific ecological risks posed by the PCDD and PCDF contamination in carp, catfish, shad and smallmouth bass from the Tittabawassee River comprise those of reduced fertility (mink and river otter), and embryo and other early life stage mortality (birds, mink, and river otter).

- To eliminate unacceptable levels of risk, the diets of mink in the Tittabawassee River and its floodplain would have to comprise less than 2% of fish from the river. Consequently, mink living in the Tittabawassee River floodplain would have to acquire more than 98% of their prey from uncontaminated food sources. This would require the animals to feed mainly outside the floodplain.

- A sensitivity analysis demonstrates that even if carp, catfish, bass and shad comprised a relatively minor fraction of the diet of piscivorous birds, and their other fish prey from the Tittabawassee River had only half the contamination levels of these four species, risks of reproductive impairment would still be high. This confirms the robustness of the risk estimations in this ERA.

- The risk levels identified by this aquatic ecological risk assessment are probably sufficiently high to result in population effects in exposed avian and mammalian piscivores.

- The main contributors to risk in piscivores through contamination of Tittabawassee River carp, catfish, shad and smallmouth bass are 2,3,4,7,8-pentachlorodibenzofuran (2,3,4,7,8-PeCDF), 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF), in that descending order.

Migratory Waterfowl Egg Collection and Analysis

In 2003, eggs of wood ducks and hooded mergansers nesting in the Shiawassee National Wildlife Refuge and from reference areas were collected and analyzed for PCDDs and PCDFs. These data showed that:

- The wood duck eggs from the Shiawassee National Wildlife Refuge had TCDD-EQ concentrations that were, on average, 2.7 times higher than those in the reference eggs. The hooded merganser eggs from the Shiawassee National Wildlife Refuge had TCDD-EQ concentrations that were, on average, 24.4 times higher than those from the reference areas.

- The TCDD-Equivalents (TCDD-EQ) in the eggs of wood ducks and hooded mergansers from the Shiawassee National Wildlife Refuge exceeded by factors of up to 49 and 122, respectively, levels that would be protective of the more sensitive bird species and by factors of up to 2.4 and 6.1, respectively, levels that would be protective of comparatively insensitive bird species. These empirical and site-specific data support the conclusions of risk to avian piscivores that were obtained in the ecological risk assessment.

- Congener data from wood duck and hooded merganser eggs from the Shiawassee National Wildlife Refuge, and the eggs of ground-foraging chickens from nearby Riverside Drive showed that 2,3,7,8-TCDF persists during food chain transfer.

Sediment Threshold Concentrations

The results of the ecological risk assessment were used to identify sediment threshold concentrations (STCs) of TCDD-EQ that would be protective of avian and mammalian piscivores. This showed that:

- The TCDD-EQ STCs for the three avian TRV categories (most, less, and least sensitive) were 10, 100, and 211 pg/g, respectively.

- The TCDD-EQ STC for mink is 12 pg/g, and for river otter is 9 pg/g.

- Sediments in the Tittabawassee River from the City of Midland downstream exceeded the STCs for birds and mammals by factors of up to more than 100.

- TCDD-EQ concentrations in 9 sediment samples from Saginaw Bay and 25 sediment samples from Saginaw River equaled or exceeded one or more of the avian and mammalian STCs, indicating that the risk posed by PCDDs and PCDFs extend downriver beyond the Tittabawassee River.

1. INTRODUCTION

In January 2003, Michigan Department of Environmental Quality (MDEQ) commissioned Dr. Hector Galbraith of Galbraith Environmental Sciences LLC (GES) to carry out an evaluation of ecological risks posed by polychlorinated hydrocarbon (PCH) contaminants in the Tittabawassee River and its floodplain. To the extent that data allow, GES was also requested to evaluate risks to ecological receptors due to PCH contaminants originating in the Tittabawassee River in areas further downstream, specifically the Saginaw River and the inner portion of Saginaw Bay. This document evaluates the magnitude of risks posed to ecological receptors exposed to PCHs in fish and sediments in the Tittabawassee River and downstream, and approximates the spatial distributions of these risks.

1.1 Report Structure

Chapter 2 of this report comprises a general introduction to the objectives and process of ecological risk assessment (ERA). It discusses in detail the ERA process framework developed by U.S. EPA (U.S. EPA, 1998), since that is the methodological approach followed in this evaluation. Chapters 3 through 5 detail the results of the various components of the ERA (*Problem Formulation*; *Analysis*; and *Risk Characterization*). In Chapter 6, the results of the ERA are used to identify sediment contaminant concentrations that are protective of ecological receptors, and to identify geographical areas of ecological risk based on these protective levels and the known distributions of contaminant concentrations. Chapter 7 discusses uncertainty associated with this ERA, while Chapter 8 lists the scientific references used in its development.

1.2 Units

Throughout this report use is made of concentrations of contaminants in biotic and abiotic media. These are typically expressed as picograms/gram (pg/g). 1 pg/g is also equivalent to a part per trillion (ppt). When the concentrations refer to soils or sediments the units are in dry weight (dw); when they refer to fish or bird egg concentrations they are in wet weight (ww), unless otherwise stated.

2. ERA – OBJECTIVES AND PROCESS

Typically, the objectives of ERA include being able to predict the likelihood that environmental stressors may pose risks to ecological resources, to anticipate where and when such risks are most likely to occur, and to determine the types and magnitudes of effects. The information obtained through ERA can then be used to help inform and focus mitigation strategies, or to help quantify trade-offs and ecological costs and benefits among alternative response actions. As an analytical problem-solving approach, ERA has mostly focused on the risks that may be posed to ecological resources by chemical contaminants, although, it can also be used to evaluate the potential risks posed by non-chemical stressors.

In essence, ERA compares measured or predicted degrees of stress on organisms or ecological systems with benchmark values that are believed, or known, to result in one or more levels of effect on the exposed organism or system. When chemical contaminants are the stressors, the process becomes one of comparing the level of stressor to which the organism(s) is exposed (the exposure concentration) to a protective toxicological benchmark established through either laboratory studies or in the field (Bartell *et al*., 1992; Calabrese and Baldwin, 1993; NRC, 2001; U.S. EPA, 1998). The ratio derived from this comparison is an index of the probability and magnitude of risk to the exposed organism(s).

While the overall approach of ecological risk assessment may be as simple as outlined above, in any actual ERA a number of assumptions may have to be made about (for example) the level of exposure, the sensitivity of the target organisms to the contaminants, the fate and transport of the contaminants, the effects of multiple contaminants, or the actual responses of the organisms to exposure. Often, contaminant-, organism-, or site-specific data do not exist and values may have to be assumed from other contaminants, organisms, or sites. Because of such assumptions, uncertainty will be associated with the parameters and results of an ERA. In response to this, and to facilitate and encourage consistency in the way that ERAs are performed, the U.S. EPA has developed a framework and guidelines (U.S. EPA, 1998). The 1998 EPA guidelines were developed by EPA staff and were extensively reviewed and modified by expert practitioners. The resulting framework and set of guidelines are now widely regarded as the "industry standards" for conducting ERA in the United States. The U.S. EPA (1998) framework comprises the risk assessment approach used in this ERA and is described below.

2.1 The U.S. EPA (1998) Ecological Risk Assessment Framework

Figure 2-1 shows a simplified form of the U.S. EPA (1998) ERA framework. It comprises three main components or stages:

Problem Formulation. In this stage the potential risk issues at the site(s) are identified, the objectives of the ERA are articulated, and an analysis plan developed. To effectively identify and describe the potential risk issues, existing information on the potential contaminants of concern (PCOCs), the exposed receptors, the types of toxicological responses that may occur due to exposure to the PCOCs, and the environmental factors that may modify the fate and transport and toxicology of the PCOCs or the behavior of the receptors are gathered and combined into a conceptual model of the site. The function of the conceptual model is to preliminarily identify and link the important components of the system, its processes, potentially exposed receptors, and the PCOCs that may result in risk to those receptors. Also identified through this process are assessment endpoints for the ERA. Assessment endpoints are expressions of the ecological resources that are to be protected and that are the focus of the ERA.

Overall, therefore, the Problem Formulation stage defines the scope, terms, and direction of the subsequent ERA. It is important to note that the whole ERA process is often iterative and the products of the Problem Formulation stage (i.e., conceptual models, assessment endpoints, and analysis plans) may be altered as data are collected during the next stage.

Analysis. The Analysis stage of an ERA has two main objectives:

1) To characterize and quantify the exposure of the ecological receptors to the PCOCs. Exposure may be quantified at several different levels according to the environmental behavior and toxicology of the contaminants. Contaminant concentrations in the diet, dietary intake rates, and receptor tissue concentrations are all often used as measures of exposure.

2) To characterize and quantify the types and degrees of toxicological responses that may occur among the receptors on exposure to the contaminants, and the sensitivities of these receptors. The outcome of this component of the Analysis stage is a stressor-response profile that addresses the following questions: what exposures to the contaminant are likely to induce toxicological responses and what exposures are protective of the organism?

The exposure and stressor-response information is combined in the final stage of the ERA (Risk Characterization) into an assessment of the level of risk that may be (or is being) incurred.

Risk Characterization. In this final stage of the ERA the products of the Analysis stage are combined to derive an estimate of risk to the exposed receptors. Such estimates may be point estimates, as when the ratio between the exposure and some response level is calculated. This estimate is termed a Hazard Index (HI). An HI greater than 1 indicates that the exposure level exceeds the response threshold and, therefore, the risk of that response has been incurred. The more that the HI exceeds 1 the greater the risk of more severe effects: an HI that only just exceeds 1 might signify that a risk exists to individual organisms, while HIs larger than that might indicate risks to larger components of the population or community.

The estimation of risk may also be probabilistic, as when mathematical simulation techniques are used to derive distributions of exposure and response. These are then combined in the Risk Characterization stage to derive probabilistic statements about risk.

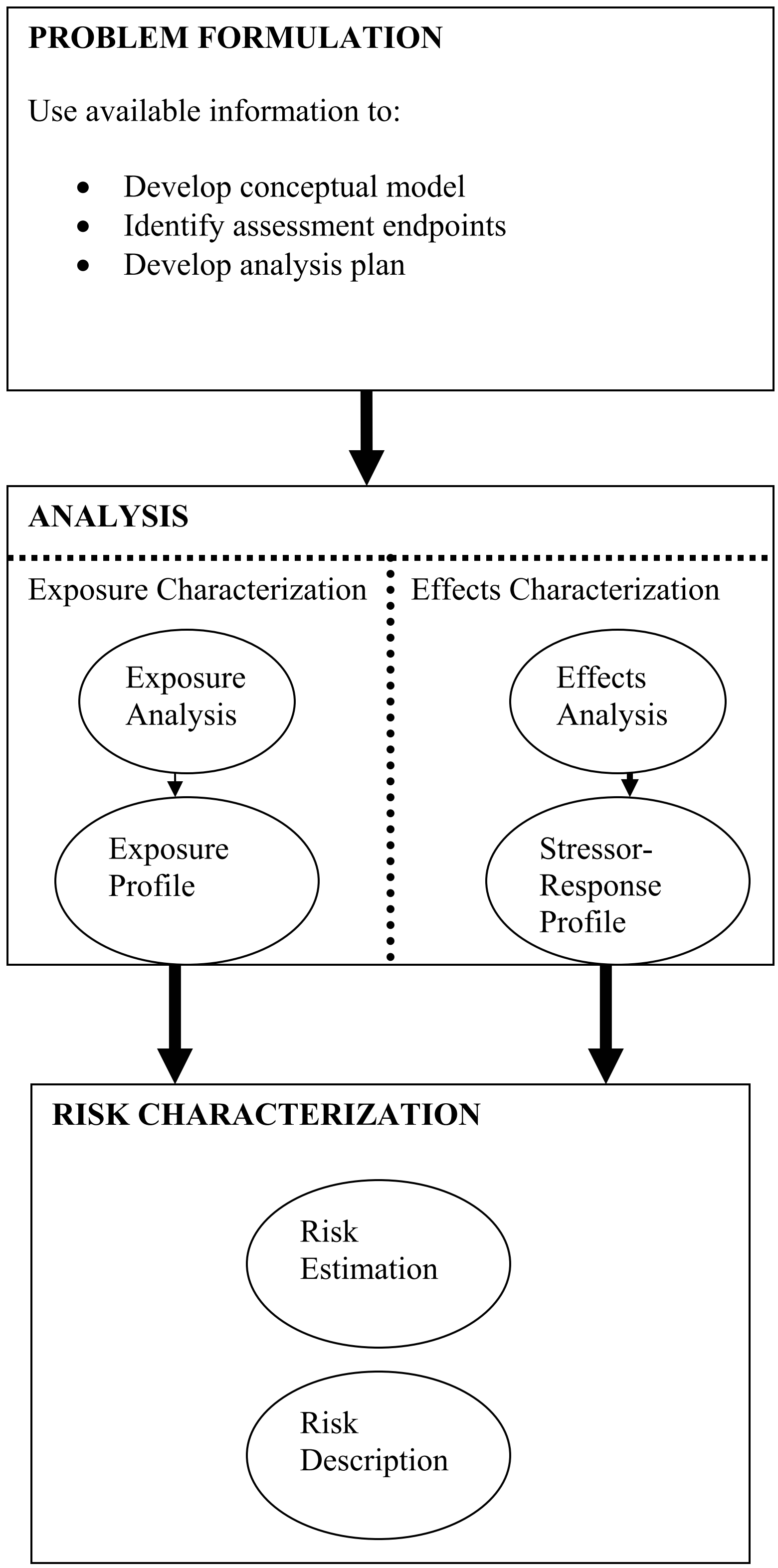


Figure 2-1. Simplified schematic of the U.S. EPA (1998) ERA framework.

2.2 Uncertainty

Uncertainty is inherent in all ecological risk assessments. It may arise from a large number of sources but is often due to the likelihood that it may not be possible to accurately predict exposure to all of the potential receptors, or that the stressor response information is not complete and assumptions must be made, or that no stressor-response information exists for the receptor and a surrogate species must be used. Regardless of its source or type, the ERA must explicitly recognize and accommodate this uncertainty. In probabilistic ERA the distributions of parameters are aimed at acknowledging and incorporating uncertainty into statements about risk. In HI risk assessments, ranges of important values (to reflect, for example, uncertainty about stressor-response values) may be used. Uncertainty factors may also be applied in HI-based ERAs in (for example) inter-species conversions or levels of effects conversions. One of the main objectives of any ERA should be to acknowledge its inherent uncertainty and then reduce that uncertainty to the extent possible. If it is not possible to reduce uncertainty to a level considered acceptable by the risk assessors and managers, the ERA must reflect this in its statements regarding the magnitude or spatial distribution of risk.

3. PROBLEM FORMULATION

3.1 The Assessment Area

Beginning in Roscommon and Ogemaw Counties in north-central Michigan, the Tittabawassee River flows south and southeast for a distance of approximately 80 miles to its confluence with the Saginaw River, which then flows east into Saginaw Bay on Lake Huron (Figure 3-1). For the first 60 miles of its course, the Tittabawassee River flows through a largely rural and agricultural landscape. Major tributaries in this upriver reach are the Tobacco, Pine, and Chippewa Rivers. At the city of Midland, the predominant land use changes as the river flows past major chemical manufacturing and processing plants, industrial and municipal wastewater discharges, and areas of urban land-use. Downriver of Midland, the river and its floodplain once again become largely rural in character, with land-use split among residential, agricultural, public parks, and other protected areas, including the Shiawassee National Wildlife Refuge. At its confluence with the Saginaw River near the City of Saginaw, the land-use near the river once again becomes largely urban and industrial. The Saginaw River floodplain is largely industrialized and urban throughout its course to Saginaw Bay, with some parklands and protected areas including the Crow Island State Game Area.

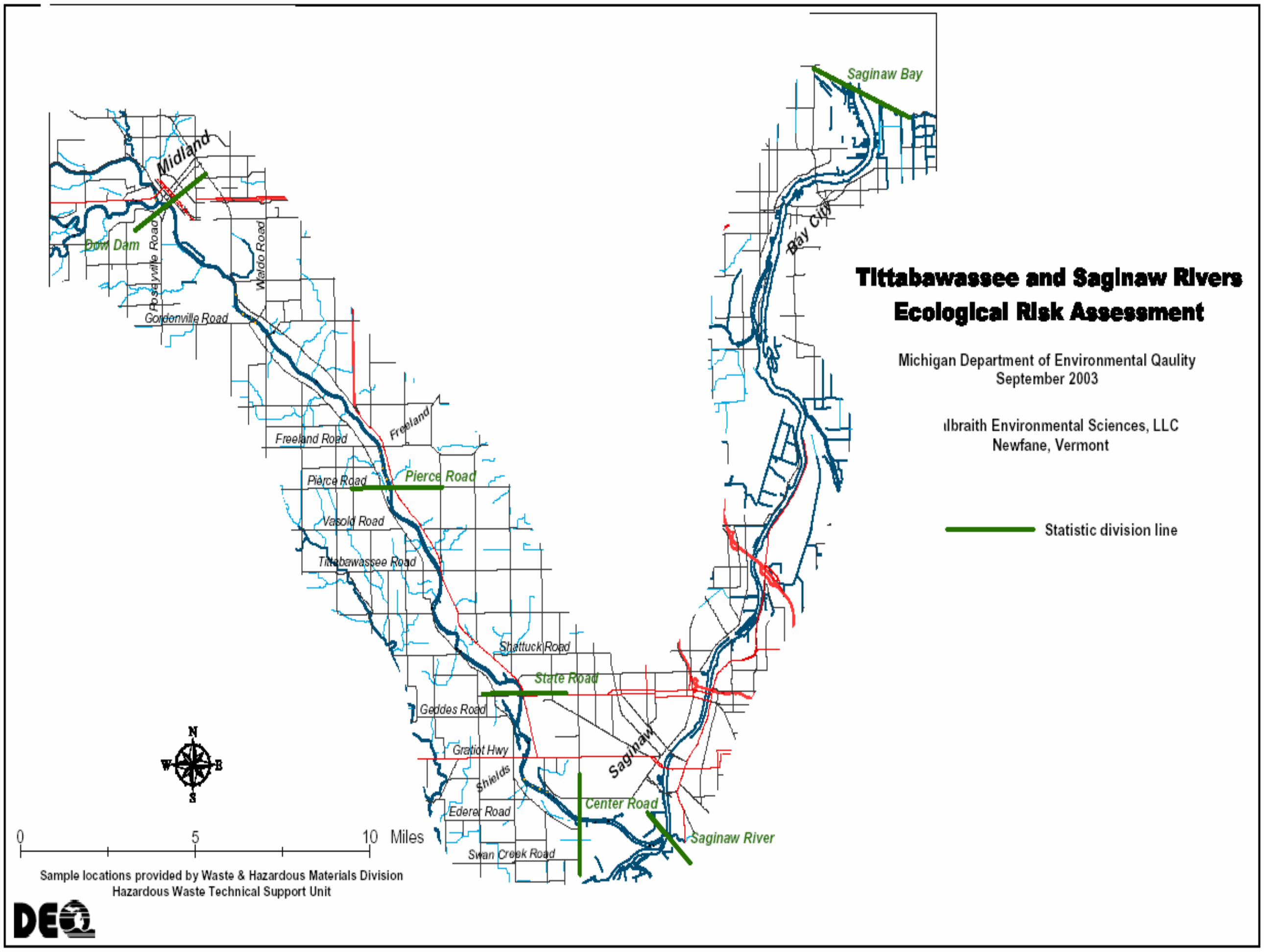


Figure 3-1. Map of the assessment area from Midland to Saginaw, and the Saginaw River and inner Saginaw Bay. This figure also shows the statistical segment lines (green lines) that have been used by MDEQ during data evaluation.

The distance from Midland to the confluence at Saginaw is approximately 22 miles and throughout most of that length, the river flows through a well-marked floodplain. In most years, parts of the floodplain are flooded by the river. In wet years, the majority of the floodplain may flood up to a depth of several feet. Thus, the river is hydrologically connected to the floodplain on a regular basis.

Upriver and downriver of the City of Midland, the river and its floodplain provide habitats suitable for a large variety of fish and wildlife species. Fish species in the river include carp (*Cyprinus carpio)*, alewife (*Alosa pseudoharengus),* walleye (*Stizostedion vitreum)*, shad (*Dorosoma cepedianum)*, smallmouth bass (*Micropterus dolomieu)*, northern pike (*Esox lucius)*, and catfish (*Ictalurus punctatus)*. These fish provide a prey base for piscivorous predators including great blue heron (*Ardea herodias)*, osprey (*Pandion haliaetus)*, belted kingfisher (*Ceryle alcyon)*, common merganser (*Mergus merganser)*, hooded merganser *(Lophodytes cucullatus)*, and bald eagle (*Haliaeetus leucocephalus).* All of these piscivorous birds were seen on visits to the river during 2002 and 2003, and some of them are known to breed along the river or on its floodplain. Riparian habitats that are available for wildlife include forested swamps, ponds, emergent wetlands, and agricultural land.

Chemical manufacturing operations began along the Tittabawassee River in the City of Midland during the 1890's. It is possible that chemical manufacturing operations with the potential to generate PCH-contaminated waste material could have begun as early as the 1920's or 1930's. However, even after the enactment of the Michigan Water Resources Commission Act in 1929, and the federal Clean Water Act in 1972, very little was known about the amount and type of PCH compounds that were being released to the air, soil, or the Tittabawassee River from these chemical manufacturing operations.

The implementation of state and federal environmental regulatory programs has historically focused on controlling, reducing, and eliminating PCH releases at the source. However, during 1984 the U.S. EPA collected soil samples at and near the Shiawassee National Wildlife Refuge, located approximately twenty miles downstream of Midland. These samples identified elevated concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Although an initial indication of a more widespread contamination problem, state and federal regulatory efforts continued to focus on reducing, eliminating, or controlling sources of PCDD/PCDF releases.

During April of 2000 soil samples were collected during the development of a wetland construction project located at the confluence of the Tittabawassee and Saginaw Rivers. Elevated PCDD/PCDF concentrations were identified. Subsequent confirmation samples collected by the MDEQ identified TCDD-EQ concentrations as high as 7,300 pg/g, over 80 times the residential direct contact criterion (RDCC) of 90 pg/g established under Part 201, Environmental Remediation, of the Michigan Natural Resources and Environmental Protection Act, 1994 PA 451, as amended, and the Part 201 administrative rules. Concern over the public and environmental health implications of these sample results prompted the MDEQ to develop and implement a phased soil sampling and assessment program in the Tittabawassee River floodplain to determine the source and extent of the contamination.

The Phase I portion of the soil sampling program was implemented during December 2000 through July 2001. The MDEQ collected 34 soil samples from five locations within a two-mile stretch of the Tittabawassee River located near the City of Saginaw. Only seven of the 34 samples contained TCDD-EQ concentrations less than the Part 201 RDCC. The Phase I sampling effort confirmed the presence of elevated PCDD and PCDF concentrations within the lower Tittabawassee River floodplain near the river's confluence with the Saginaw River.

The MDEQ also collected and analyzed Tittabawassee River sediment samples during spring/summer 2001. The objective of the MDEQ Sediment Study was to characterize concentrations of contaminants in Tittabawassee River sediments both upstream and downstream of Midland. PCDDs and PCDFs were analyzed as part of this study. Surface sediment samples were collected from the Chippewa River, Pine River, and Tittabawassee River beginning immediately upstream of Midland and continuing downstream to its confluence with the Saginaw River. Sediment cores were collected in selected areas. Some floodplain soil samples were also collected for analysis. These samples confirmed that elevated concentrations of PCDDs and PCDFs are pervasively present in sediment and floodplain soil downstream of Midland. Any variability of contaminant concentrations in river sediment samples was determined to be a result of the variability of river water flow and site-specific sediment deposition characteristics.

An expanded Phase II flood plain soil sampling program was implemented by the MDEQ during 2002. Floodplain soil samples were collected from sixteen locations extending from eight miles upstream of Midland downstream to shoreline areas located along the Saginaw River and the inner portions of Saginaw Bay. Phase II results confirmed that PCDD/PCDF contamination of flood plain soil is extensive, extending downstream from Midland to shoreline areas located within the inner portions of Saginaw Bay. The highest concentrations were consistently observed within the twenty-two miles of the Tittabawassee River floodplain downstream of Midland. Elevated PCDD/PCDF concentrations were identified at one location to a depth of four feet below the ground surface.

As of the date of this report, the State of Michigan has entered into a waste management license with the Dow Chemical Company (Dow) under the authority of the federal Resource Conservation and Recovery Act (RCRA). The license provides for the investigation, interim response, and full remediation of dioxin contamination, and other contamination, that may have been released from the Dow Midland manufacturing complex to the Tittabawassee River sediment and flood plain soil, as well as Midland soil. Dow is in the initial stages of implementing license conditions.

The Tittabawassee River between Midland and the confluence with the Saginaw River is the primary area of interest in this ERA. However, the analysis also extends into the Saginaw River and Saginaw Bay, as the data allow.

3.2 Contaminants in the Assessment Area

Floodplain soil and riverbed sediment sampling and analysis have shown that beginning at Midland and extending downriver to the confluence with the Saginaw River the Tittabawassee River and its floodplain are contaminated to above background levels with PCHs. Upriver of Midland, PCH concentrations in the floodplain soil are either low or non-detectable (MDEQ, 2002; MDEQ, 2003). The soil and sediment samples collected by the MDEQ from the Tittabawassee River and its floodplain upstream and downstream of Midland indicate that polychlorinated biphenyls (PCBs) are not present in high concentrations. Similarly, pesticides were detected at only a few sample sites and at very low concentrations (MDEQ, 2002).

Unlike PCBs, PCDDs and PCDFs were found at elevated concentrations in all floodplain soil or sediment samples that were collected downriver of Midland (MDEQ, 2002; MDEQ, 2003). Much lower or non-detectable concentrations were found upriver of Midland. In an earlier study, Amendola and Barna (1986) also reported PCDD concentrations at up to 16,000 pg/g in the Tittabawassee River sediments downriver of Midland, but did not detect PCDDs upriver of Midland. That these contaminants were also being transferred to and accumulated in foodchains was confirmed by analyses of fish collected by MDEQ from the Tittabawassee River in 2002, from analysis of the eggs of chickens (*Gallus domesticus*) foraging in the floodplain in 2002 (MDEQ, 2003), and from analyses of the eggs of wood ducks (*Aix sponsa*) and hooded mergansers nesting in the Shiawassee National Wildlife Refuge in 2003 (USFWS and MDEQ unpublished data). The wood duck and hooded merganser samples contained higher concentrations of PCDDs and PCDFs than in reference areas elsewhere in Michigan.

Preliminary analyses of these data by MDEQ and by GES indicated that PCDDs and PCDFs may be present in sufficient concentrations in the Tittabawassee River sediments and biota to pose risks to ecological receptors. Because of this, and their intrinsic toxicity and environmental behavior (see Section 3.2.1), PCDDs and PCDFs in the Tittabawassee River are the focus of this ERA.

3.2.1 Structure, toxicity, and environmental behavior of PCDDs and PCDFs

PCDDs and PCDFs are classes of compounds consisting of large numbers of individual isomers or congeners (75 and 135, respectively). The skeleton of the PCDD molecule consists of two phenyl rings joined by two oxygen bridges. That of the PCDF molecule comprises two phenyl rings joined by one oxygen bridge and one single bond (Figure 3-2). The individual congeners of PCDDs and PCDFs differ in their patterns of chlorine substitution; examples are shown in Figure 3-2. The degree and pattern of substitution affects the stereochemistry of the congener, and is responsible for inter-congener differences in environmental behavior and toxicity. Congeners that are substituted only at the 2, 3, 7, or 8 positions (Figure 3-2) are lipophilic, structurally rigid, and resistant to environmental degradation. They also readily bind to the crucial AhR enzyme receptor in vertebrates, the molecular event that is responsible for the adverse toxicological effects of many PCDDs and PCDFs (Bosveld, 1995; NRC, 2001; Safe, 1993; Van den Berg *et al*., 1994). Because they are lipophilic and resist degradation and metabolism, they readily bioaccumulate in food chains and may biomagnify at successive trophic levels. 2,3,7,8-TCDD is one of the most toxic compounds yet tested, eliciting mortality in some organisms at concentrations as low as a few pg/g in tissues (Eisler, 1986). Congeners without at least the 2,3,7, and 8 positions substituted are less stable, more susceptible to degradation by metabolic and environmental processes, and bind less readily to the AhR receptor. In this report PCDDs and PCDFs will mean 2,3,7,8-substituted isomers, unless otherwise noted.

Because of their toxicologies, biochemistries, and environmental chemistries, PCDDs and PCDFs can pose risks to ecological receptors at relatively low exposures. Organisms at the tops of food chains (i.e., vertebrate predators) generally experience higher levels of exposure than those at lower trophic levels. Also, early life stages of organisms are more sensitive than older life stages. Thus, their adverse effects in laboratory and free-ranging populations are most often manifested in the young or embryos of top predators (e.g., Van den Berg *et al*., 1994; Giesy *et al*., 1994a; Nosek *et. al*., 1993; Powell *et al*., 1996; Van den Berg *et. al*., 1994; White and Hoffman, 1995. Summaries in: Eisler, 1986; Hoffman *et al*., 1996).

3.3 Conceptual Models

The purpose of conceptual models in ERA is to describe the relationships among environmental media, contaminants, and exposed organisms, and to trace the pathways through which the ecological receptors may be exposed to the contaminant(s). By doing so, the conceptual model informs and directs the risk analysis. Although the river and floodplain are hydrologically linked in the assessment area (see Section 3-1 above), and contaminants flow between the riverine and terrestrial environments, for the sake of clarity the contaminant-media-receptor interrelationships have been expressed as two connected conceptual models in Figures 3-3 and 3-4. Since this report addresses risks posed by contaminants in the aquatic environment, Figure 3-3 is the relevant conceptual model. Figure 3-4 is included only to show that risk may be transferred between the aquatic and terrestrial environments.

In freshwater aquatic systems (including the Tittabawassee River) most of the PCDDs and PCDFs will be in the sediments, where they bind to the organic carbon fraction (Fletcher and McKay, 1993; Rifkin and Bower, 1994; NRC, 2001; U.S. EPA, 1993a). From the sediments they may be passed to sediment-dwelling invertebrates by direct contact and through the diet, and thence to fish that consume these invertebrates (Figure 3-3). Figure 3-3 also shows that bottom-dwelling fish such as carp or catfish may accumulate PCDDs and PCDFs through direct contact with the sediments or through ingesting contaminated sediments with their diet. Since the carp or catfish may be the prey of piscivorous predators such as bald eagles or river otters, the top predators in the food chains may become exposed.

Another exposure route to these top predators is due to the fact that not all of the organic contaminants are "locked" in the sediments. PCDDs and PCDFs partition between sediments and the overlying water column and occur both as freely dissolved forms and bound to suspended particulates, colloids, and humic substances. PCDDs and PCDFs in the water column can be accumulated directly by phytoplankton and zooplankton, and by zooplankton through the ingestion of the phytoplankton. Forage fish and predatory fish may then be exposed through direct gill uptake and from their diet. Bird and mammal predators may then be exposed by consuming forage and predatory fish (Figure 3-3).

Because of their strong tendency to partition into organic carbon in sediments and lipids in organisms, the majority of the PCDDs and the PCDFs that are passed up the aquatic foodchain are likely to do so via the sediment-based dietary pathway.

3.4 Assessment Endpoints

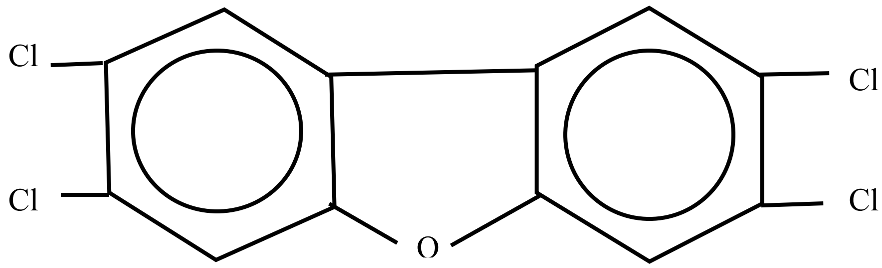
Assessment endpoints have been chosen for the aquatic ERA based on the known sensitivities of organisms at different levels in food chains and life stages to PCDDs and PCDFs (predators and early life stages being most vulnerable).

The assessment endpoints for this aquatic ERA are:

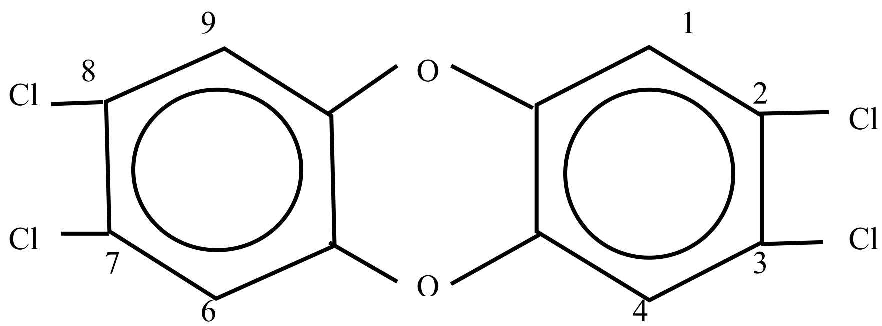
- Protection of avian piscivore embryos
- Protection of mammalian piscivore reproduction and embryos

Because these endpoints represent protection of the ecological receptors that are likely to be most vulnerable to PCDDs and PCDFs within the assessment area, they are likely to be protective of the other, less vulnerable, exposed ecological resources.

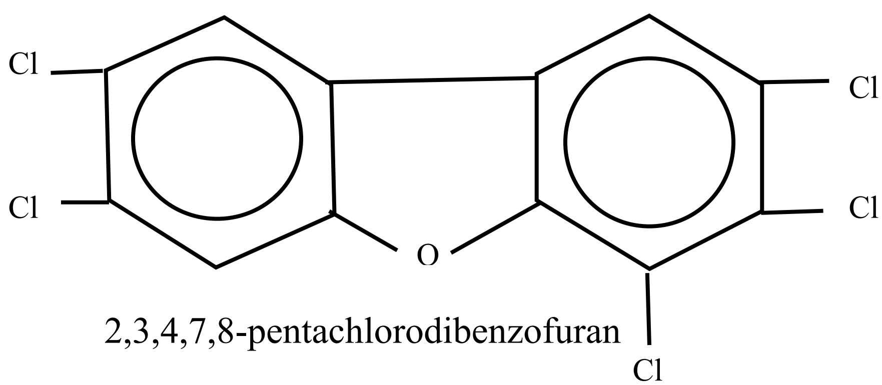
Assessment endpoints are general, non-quantitative statements about the resources that are to be protected through the ERA process. They do not provide quantitative targets or criteria on which the ERA can be based. However, they are important in that they provide focus for the ERA and provide the basis from which quantitative *measurement endpoints* can be established. These measurement endpoints are described in Sections 4.1 and 4.2 of this ERA.



2,3,7,8-tetrachlorodibenzofuran



2,3,7,8-tetrachlorodibenzo-*p*-dioxin



2,3,4,7,8-pentachlorodibenzofuran

Figure 3-2. Molecular structures of PCDD and PCDF congeners

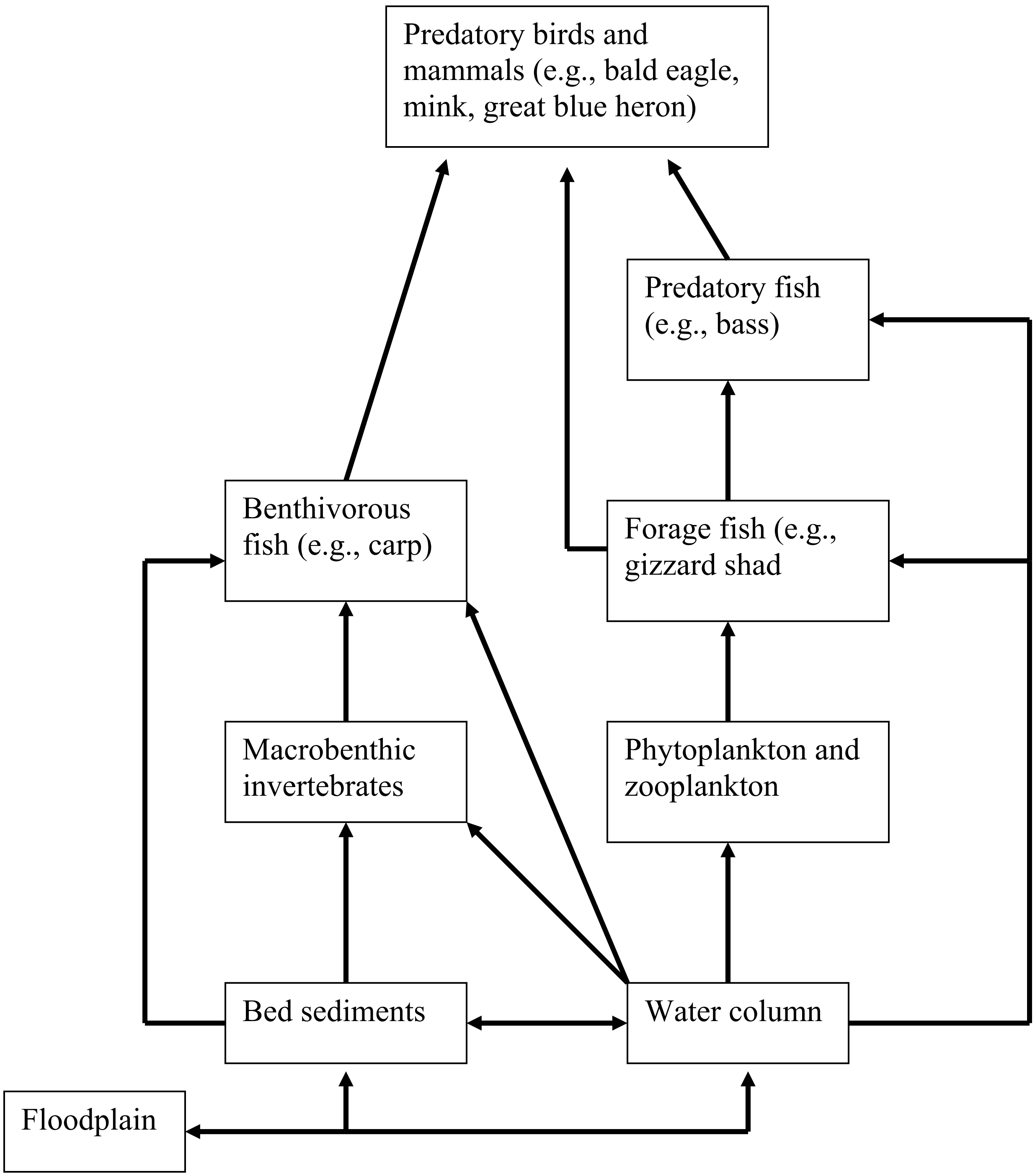


Figure 3-3. Paths of dietary and direct-contact transfer of PCHs in the Tittabawassee River aquatic food web.

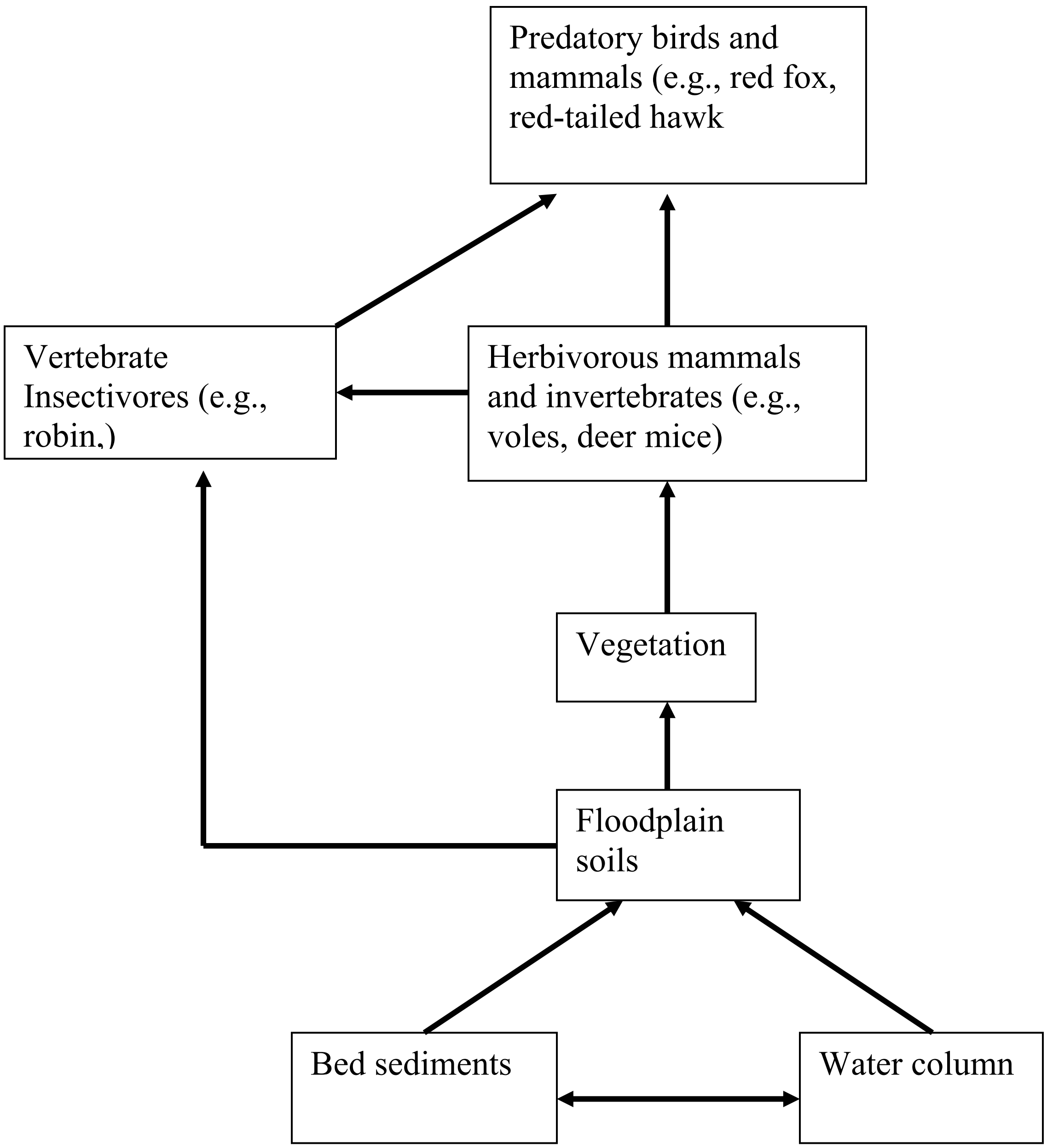


Figure 3-4. Paths of dietary transfer of PCHs in the Tittabawassee River floodplain terrestrial food web.

4. ANALYSIS

This section describes the approaches followed and the values obtained in the determination of two important components of ecological risk evaluation:

- Developing stressor response relationships. In this ERA this translates into identifying the exposures of the target organisms to the contaminants that are likely to be associated with toxicological responses (henceforward referred to as toxicity reference values or "TRVs"). The resulting values are the measurement endpoints described in Section 3.4.

- Estimating the exposure of the target organisms to PCDDs and PCDFs

Each of these stages is discussed separately for the avian and mammalian piscivores.

4.1 Avian Piscivores

Toxicity Reference Values (TRVs)

The most sensitive avian life stage to PCH toxicity is the embryo (Gilbertson *et al*., 1991; Kubiak and Best, 1991; U.S. EPA, 1993a; Giesy *et al*., 1994a; Barron *et al*., 1995; Hoffman *et al*., 1996; Hoffman *et al*., 1998). Because of this well-established early life stage sensitivity, avian embryo viability was selected as an endpoint in this assessment. To determine avian embryo TRVs, the scientific literature was reviewed to identify egg concentrations of PCHs known, from previous studies, to have resulted in adverse effects on embryo survival and hatching success. The data obtained (from field studies and laboratory egg injection studies) could be categorized as any of the following:

- Frank effects concentrations (FECs), i.e., egg concentrations associated with reductions in embryo survival and hatchability but not directly translatable into dose-response relationships
- LD50s - the concentrations in the eggs associated with 50% embryo mortality (one LD98 value was also found)
- Lowest observed adverse effects concentrations (LOAECs), i.e., the lowest egg concentration associated with reduced embryo survival
- No observed adverse effects concentrations (NOAECs), i.e., the highest concentration that did not result in reduced survival.

Different PCDD and PCDF congeners, although they may have similar toxicological modes of action, have different toxicities to ecological receptors. Thus, the PCDD or PCDF concentration in a sample comprising a complex mixture of congeners may reveal relatively little about its toxicity. The most robust current approach to evaluating the potential risks posed by such mixtures is to estimate the toxicities of the congeners relative to that of 2,3,7,8-TCDD (the most well-studied and generally the most toxic of the dioxin congeners). To accomplish this, the concentration of each congener is converted to the equivalent 2,3,7,8-TCDD concentration (the TCDD-Equivalent or TCDD-EQ) using toxicity equivalence factors (TEFs). TEFs are the ratios of the toxicities of the congeners relative to that of 2,3,7,8-TCDD. In this ERA, the TEFs developed by the World Health Organization (Van den Berg *et al*., 1998) are used, together with others if necessary. Because these compounds act through the same mechanism, their toxicity is generally additive in environmentally relevant mixtures (Safe *et al*., 1990; Van den Berg *et al*., 1998). Thus, the total TCDD-EQ exposure is estimated by summing the TCDD-EQs for all the PCDD and PCDF congeners and any other compounds that share the same mechanism of action. Thus, the final TCDD-EQ value is a measure of the total toxicity of the mixture relative to 2,3,7,8-TCDD, and can be compared with toxicity reference values for that congener.

The values obtained in this review of avian toxicity data were converted to TCDD-EQs using WHO avian TEFs (Van den Berg *et al*., 1998), except where the toxicological agent was 2,3,7,8-TCDD or the data were derived from H4IIE (bioassay) studies. In such cases the reported concentrations were used. The results are shown in Table 4-1. Where FECs, LD50s, or LD98s are reported, but LOAECs or NOAECs are not, the reported concentrations are converted in Table 4-1 to LOAECs and NOAECs by applying uncertainty factors. A factor of 10 was used to convert FEC or LD50 values to LOAECs and another factor of 10 to convert them to NOAECs. Values reported as LOAECs are converted to NOAECs by applying an uncertainty factor of 10. The use of uncertainty factors conforms to U.S. EPA guidance for conducting dioxin ecological risk assessments (U.S. EPA, 1993a) and they have been used in previous important Great Lakes PCH ecological risk assessments (Giesy *et al*., 1994a, b, and c).

The data in Table 4-1 show that there is wide variation in intrinsic sensitivity to TCDD-EQs among birds. The white leghorn chicken is the most sensitive species tested thus far, with LD50 egg concentrations in the range 40-430 pg/g TCDD-EQ. This translates into a NOAEC range of <1 – 4.3 pg/g TCDD-EQ. Based on a field study, White and Seginak (1994) and White and Hoffman (1995) established that wood ducks were also comparatively sensitive, with a LOAEC of 20-50 pg/g, which translates into a NOAEC of 2-5 pg/g TCDD-EQ. Great blue heron LOAECs and NOAECs range between 52 and 100 pg/g, and 5.2 and 17.6 pg/g, respectively (Hart *et al*., 1991; Henshel *et al*., 1995). NOAECs measured and extrapolated for Forster's tern (*Sterna forsteri*) range from 5.4 to 59 pg/g TCDD-EQ (Kubiak *et al*., 1989; Harris *et al*., 1993). The other species in Table 4-1 are, apparently, less sensitive with NOAECs that are generally above 50 or 100 pg/g TCDD-EQ.

Table 4-2 lists avian egg TCDD-EQ NOAECs that have been used in previous PCH ecological risk assessments. These are typically less than 100 pg/g.

Table 4-1. Literature-derived and extrapolated avian egg TCDD-EQ LOAECs and NOAECs (where necessary WHO avian TEFS used to convert to TCDD-EQ). Concentrations in pg/g, wet weight.						
Species	**Method**	**Analytes and Metric Measured**	**TCDD-EQ**	**TCDD-EQ LOAEC**	**TCDD-EQ NOAEC**	**Reference**
Wood duck *Aix sponsa*	Field study	PCDD/PCDF LOAEC	20-50	20-50	2-5*	White and Seginak, 1994
						White and Hoffman, 1995
Great blue heron *Ardea herodias*	Field study	PCDD/PCDF FEC	519	52	5.2*	Hart *et al.*, 1991
	Field study	PCDD/PCDF NOAEC	17.6		17.6	Hart *et al.*, 1991
	Field study	PCDD/PCDF LOAEC	10-100	100	10*	Henshel *et al.*, 1995
Forster's tern *Sterna forsteri*	Field study	PCDD/PCDF/PCB NOAEC	59	59	59	Kubiak *et al.*, 1989
	Field	FEC	542	54*	5.4*	Kubiak *et al.*, 1989
	Field study	PCB FEC	567	57*	5.7*	Harris *et al.*, 1993
Common tern *Sterna hirundo*	egg injection	PCB 126/77 LD50	10,400	1,040*	104*	Hoffman *et al.*, 1995
Double-crested cormorant *Phalacrocorax auritus*	egg injection	TCDD FEC	250-4,000	1,000*	100*	Powell *et al.*, 1997a
	egg injection	TCDD LD50	4,000	400*	40*	Powell *et al.*, 1998
	Field study	H4IIE TCDD-EQ NOAEC	>35		100	Tillitt *et al.*, 1992
	Field study	H4IIE TCDD-EQ LOAEC	100-200	100-200	10-20*	Tillitt *et al.*, 1992
Pheasant *Phasianus colchicus*	egg injection	TCDD LOAEC	100-1000	<1000	100*	Nosek *et al.*, 1993
		TCDD LD50	1,354-2,182	135-218*	13.5-21.8*	Nosek *et al.*, 1993
		TCDD-EQ LD98	3,300	33*	3.3*	Nosek *et al.*, 1992
		PCB 126 LD50	5000-50,000	500-5,000*	50-500*	Brunstrom and Reutergardh, 1986
Turkey *Meleagris gallopavo*	egg injection	PCB 126 LD50	40,000	4,000*	400*	Brunstrom and Lund, 1988

Table 4-1 continued						
Species	**Method**	**Analytes and Metric measured**	**TCDD-EQ**	**TCDD-EQ LOAEC**	**TCDD-EQ NOAEC**	**Reference**
Bobwhite *Coturnix coturnix*	egg injection	PCB 126 LD50	2,400	240*	24*	Hoffman *et al*., 1996
American kestrel *Falco sparverius*	egg injection	PCB 126 LD50	6,500*	650*	65*	Hoffman *et al*., 1998
Mallard *Anas platyrhynchos*	egg injection	PCB 126 LD50	>250,000	>25,000*	>2500*	Brunstrom, 1988
Herring gull *Larus argentatus*	egg injection	PCB 126			>2,500	Brunstrom, 1988
Domestic goose *Anser anser*	egg injection	PCB 126				Brunstrom, 1988
Eastern bluebird *Sialia sialis*	egg injection	TCDD LD50	1,000-10,000	100-1,000*	10-100*	Martin *et al*., 1989
		TCDD LOAEC	10,000	10,000	1,000*	Thiel *et al*., 1989
Black-headed gull *Larus ridibundus*	egg injection	PCB 126 LD50	<50,000	<5,000*	<500*	Brunstrom and Reutergardh, 1986
White leghorn chicken *Gallus domesticus*	egg injection	TCDD LD50	115	11.5*	1*	Henshel, 1993
	egg injection	TCDD LD50	180	18*	2*	Henshel , 1993
	egg injection	PCB 126 LD50	230	23*	2.3*	Powell *et al*., 1996
	egg injection	TCDD LD50	150	15*	1.5*	Powell *et al*., 1996
	egg injection	PCB 126 LD50	245	24*	2.4*	Powell, 1995
	egg injection	TCDD LOAEC	10	10	1*	Henshel, 1993
	egg injection	PCB 126 LD50	40	4	0.4*	Hoffman *et al*., 1995 and 1998
	egg injection	PCB 77 LD50	130	13	1.3*	Hoffman *et al*., 1995 and 1998
	egg injection	PCB 126 LD50	430	43	4.3*	Brunstrom and Andersson, 1988
	egg injection	PCB 126 LD50	320	32	3.2*	Brunstrom and Andersson, 1988
Rock dove *Columba livia*	egg injection	TCDD LOAEC	3,000	3,000	300*	Janz and Bellward, 1996

* indicates that an uncertainty factor was used in derivation of value

Table 4-2. Avian egg TCDD-EQ NOAECs (pg/g, ww) used in previous ecological risk assessments for PCBs, dioxins, or furans		
Species	**NOAEC**	**Authority**
Bald eagle	20	Kubiak and Best, 1991
Bald eagle	7	Giesy *et al*., 1994c
Bald eagle	7	Bowerman *et al*., 1995
Bald eagle	114	Derived by Bowerman *et al*., 1995 from U.S. EPA, 1993.
American kestrel	40-70	Bowerman *et al*., 1995
American kestrel	70	Kemler *et al*., 2000

In this ERA, rather than focus on particular bird species as indicators of risk to PCH contamination, we have developed three NOAEC categories that are consistent with and reflect the range of variability seen in Table 4-1**:**

Most Sensitive bird species	>5-50 pg/g TCDD-EQ
Less Sensitive species	>50-100 pg/g TCDD-EQ
Least Sensitive species	>100 pg/g TCDD-EQ

Thus, bird egg TCDD-EQ concentrations that exceed 5 pg/g (but that are less than 50 pg/g) pose risks to embryo viability in the Most Sensitive species. Egg TCDD-EQ concentrations that exceed 50 pg/g (but that are less than 100 pg/g) pose similar risks of embryo viability to the Less and the Most sensitive species, and egg TCDD-EQ concentrations that exceed 100 pg/g pose risks to embryo viability to all three sensitivity categories. The latter is not meant to imply that all comparatively insensitive species may be at risk from concentrations above 100 pg/g; some species (e.g., mallard) may have NOAECs an order of magnitude higher than 100 pg/g. Nevertheless, it can be expected that this is the threshold where risks to this sensitivity category may begin to be incurred. Thus, the three TRVs used in this ERA are 5, 50, and 100 pg/g for Least, Less, and Most sensitive species, respectively.

In the assessment area, the category Most Sensitive might include bald eagle, great blue heron, and wood ducks; Less Sensitive species could include American kestrel or Forster's tern, while Least Sensitive species could include mallard. The actual sensitivities of the vast majority of bird species that occur in the assessment area are unknown, since they have not been tested in the laboratory or in the field. However, by using the three TRV categories identified above, the risks to these species of uncertain sensitivity can be inferred.

Diet – Egg Biomagnification Factors

In the aquatic food web component of this ecological risk assessment, the embryonic exposure of piscivorous birds to PCDDs and PCDFs is inferred from known concentrations in fish in the Tittabawassee River. PCH concentrations in the eggs of piscivorous bird species are extrapolated from the fish tissue concentrations using Biomagnification Factors (BMFs). BMFs are ratios between the PCH concentrations in the fish diet and the bird eggs. By multiplying the fish PCH concentration by the BMF, the egg concentration can be estimated. This must be done on a congener basis since PCH congeners differ in their propensities to be transmitted from diet to egg.

Table 4-3 lists fish tissue – bird egg BMFs from field studies reported in the scientific literature. Clearly, the BMFs vary across the congeners studied and between studies. In this ecological risk assessment we extrapolate representative BMFs from the results in Table 4-3. These are shown in Table 4-4.

Table 4-3. Fish – bird egg BMFs reported in the scientific literature

Congener	**Fish Tissue concentration (pg/g)**	**Egg concentration (pg/g)**	**BMF**	**Authority**
2,3,7,8-TCDD	4.0	83	20.7	Braune and Norstrom, 1989
2,3,7,8-TCDD			37	Kubiak *et al*., 1989
2,3,7,8-TCDD-EQ	11	1065	98[c]	Kubiak and Best, 1991
2,3,7,8-TCDD-EQ	57	1065	19[c]	Kubiak and Best, 1991
2,3,7,8-TCDD-EQ			31.3[d]	Jones *et al*., 1994
1,2,3,7,8-PeCDD	1.0	9.7	9.7	Braune and Norstrom, 1989
1,2,3,6,7,8-HxCDD	1.0	16	16	Braune and Norstrom, 1989
2,3,7,8-TCDF	2.0	ND	<1	Braune and Norstrom, 1989
2,3,7,8-TCDF			"negligible"	Kubiak *et al*., 1989
2,3,4,7,8-PeCDF	2.0	8.9	4.5	Braune and Norstrom, 1989
2,3,4,7,8-PeCDF			64.6[a]	Van den Berg *et al*., 1987
1,2,3,4,6,7-HxCDF	ND	4.2	>4[b]	Braune and Norstrom, 1989
1,2,3,6,7,8-HxCDF	ND	4.0	>4[b]	Braune and Norstrom,1989

[a] this study calculates a fish – cormorant liver BMF. This is converted to fish to egg BMF using herring gull liver to egg ratio of 0.19 (Braune and Norstrom, 1989). [b] Calculated assuming a detection limit of 1 pg/g. [c] The BMF of 98 is derived from alewife to bald eagle egg data, while the BMF of 19 is based on northern pike to bald eagle egg data. [d] Mean from 5 Great Lakes sites (range 11.7 – 56.8).

Table 4-4. BMFs used in this ecological risk assessment	
Congener	**BMF**
2,3,7,8-TCDD	29[a]
1,2,3,7,8-PeCDDD	9.7
1,2,3,6,7,8-HxCDD	16
2,3,4,7,8-PeCDF	10[b]
2,3,7,8-TCDF	1
1,2,3,4,6,7-HxCDF	4[c]
1,2,3,6,7,8-HxCDF	4[c]

[a]Calculated as the mean of the values in Table 4-3. [b]Assumed as being between the values reported in Table 4-3, but closer to the low (4.5) value. [c]Assumed to be the lowest possible value.

The information presented in Table 4-3 suggests that 2,3,7,8-TCDF may not be biomagnified from fish to bird eggs. This has been explained by invoking a greater tendency for this congener to be metabolized and excreted by birds. However, this conclusion is surrounded by a great deal of uncertainty since so few field studies of food chain transfer have been performed for this congener. During the course of this study, 85 individual summer-resident fish were collected from the Tittabawassee River. In addition, eggs were collected from 5 wood duck and 4 hooded merganser nests on the Shiawassee National Wildlife Refuge in 2003. If 2,3,7,8-TCDF was not being bioaccumulated by these birds, the congener mix in the fish, and eggs should differ in that 2,3,7,8-TCDF would be represented at a lower level in the eggs compared to the fish. The results are shown in Table 4-5. Although sample sizes are small, the congener compositions in the fish and the duck eggs suggest that 2,3,7,8-TCDF was not selectively eliminated during food chain transfer from fish to bird eggs. In fact there is evidence that 2,3,7,8-TCDF is biomagnified relative to the other two congeners. Based on this, it was assumed in this ecological risk assessment that the BMF for 2,3,7,8-TCDF equals 1.

Table 4-5. Percent contributions of PCDD and PCDF congeners to total TCDD-EQ in fish, wood duck and hooded merganser eggs from Tittabawassee River floodplain (WHO avian TEFs).			
Sample	**2,3,7,8-TCDD**	**2,3,7,8-TCDF**	**2,3,4,7,8-PeCDF**
Fish (n=85)	23.9	11.9	60.5
Wood duck (n= 5)	2.3	72.0	20.8
Hooded merganser (n=4)	5.4	63.7	21.6

The BMF selected for this study for 2,3,4,7,8-PeCDF (10) is between the Braune and Norstrom (1989) and Van den Berg *et al*. (1987) values reported in Table 4-3. It has been assumed that the actual value would be closer to the smaller (Braune and Norstrom) value. Hence, a BMF of 10 was selected.

Table 4-6 shows TCDD-EQ fish – egg BMFs that have been used in previous ecological risk assessments in the Great Lakes. These vary between 10 and 178, depending on the fish species.

Table 4-6. Fish – bird egg BMFs used in previous Great Lakes ecological risk assessments

Contaminant	**Bird Species**	**Fish Species**	**BMF**	**Authority**
TCDD-EQ	Bald eagle	Unknown	19	Giesy et al., 1994c
TCDD-EQ	Bald eagle	northern pike	19	Kubiak and Best, 1991
TCDD-EQ	Bald eagle	Alewife	97	Kubiak and Best, 1991
TCDD-EQ	Bald eagle	Chinook	19	Kubiak and Best, 1991
TCDD-EQ	Bald eagle	white sucker	178	Kubiak and Best, 1991
TCDD-EQ	Bald eagle	Carp	10	Kubiak and Best, 1991

Estimating PCH Concentrations in Bird Eggs from Concentrations in Fish Tissues

During the summer of 2002 Michigan Department of Natural Resources, with MDEQ assistance, collected fish from the Tittabawassee River from just downstream of Midland to just upstream of the Saginaw River. Carp, shad, smallmouth bass, and catfish were collected, as availability allowed, and analyzed for PCDDs and PCDFs (Table 4-7). These data comprise the basis of this ERA. Using the fish tissue PCH concentrations (Table 4-7), the BMFs in Table 4-4, and WHO avian TEFs, the TCDD-EQ in fish tissues and piscivorous bird eggs in the assessment area were estimated (Tables 4-7 and 4-8, respectively). The fish tissue TCDD-EQs range between 73 pg/g (bass) and 307 pg/g (carp). Applying the BMFs from Table 4-4 results in TCDD-EQ egg concentrations that range between 333 pg/g and 2222 pg/g (Table 4-8). These are the exposure levels that are compared with avian egg TRVs in Section 5 of this report to derive estimates of risk (assuming that these four species of fish from the Tittabawassee River are 100% of the diet).

Table 4-7. PCDD and PCDF congener concentrations (pg/g, ww) and TCDD-EQ (in parentheses) in tissues of fish collected by MDEQ in 2002 from the Tittabawassee River. TCDD-EQ calculated using tissue concentrations and WHO avian TEFs.										
	2,3,7,8-TCDD	**1,2,3,7,8-PeCDD**	**2,3,7,8-TCDF**	**1,2,3,7,8-PeCDF**	**2,3,4,7,8-PeCDF**	**1,2,3,4,7,8-HxCDF**	**1,2,3,6,7,8-HxCDF**	**1,2,3,7,8,9-HxCDF**	**Other congeners**	**Total TCDD-EQ**
Carp N=26	10.8 (10.8)	5.3 (5.3)	101.3 (101.3)	64.0 (6.4)	174.9 (174.9)	48.1 (4.8)	15.5 (1.5)	25.2 (2.5)	56.5 (<1)	307
Catfish N=24	9.4 (9.4)	5.4 (5.4)	5.9 (5.9)	<1 (<1)	59.8 (59.8)	6.0 (<1)	2.0 (<1)	33.2 (3.3)	57 (<1)	85
Shad N=23	4.2 (4.2)	1.5 (1.5)	195.5 (195.5)	25.4 (2.5)	30.3 (30.3)	7.3 (<1)	2.8 (<1)	9.8 (1.0)	106.2 (<1)	236
Bass N=12	3.8 (3.8)	1.1 (1.1)	40 (40)	<1 (<1)	17.1 (17.1)	3.5 (<1)	1.5 (<1)	2.1 (<1)	3.7 (<1)	73

Table 4-8. TCDD-EQ (pg/g, ww) in eggs of avian piscivores estimated based on consumption of different fish species from the Tittabawassee River.					
	Carp	**Catfish**	**Shad**	**Bass**	**Mean of all fish**
Egg TCDD-EQ	2222	930	638	333	1031

Table 4-9 shows TCDD-Eqs (calculated using WHO avian TEFs) in wood duck and hooded merganser eggs collected from the Shiawassee National Wildlife Refuge in 2003, together with eggs from a reference area (Rose Lake State Game Area, Michigan). These data show that both species have substantially higher egg TCDD-EQs at the Shiawassee NWR than at the reference area. Despite the small sample sizes, they also show that the egg concentrations at the Shiawassee NWR are consistent with those predicted in Table 4-8. The maximum TCDD-EQ in only four hooded merganser eggs exceeded 600 pg/g. This is approaching the concentrations predicted in Table 4-8.

Table 4-9. TCDD-EQ in wood duck and hooded merganser eggs from the Shiawassee National Wildlife Refuge and a reference area (Rose Lake State Game Area, Michigan). TCDD-EQ calculated using WHO avian TEFs. All concentrations are pg/g fresh wet weight.		
	Mean Concentration	**Range**
Wood Duck (Shiawassee, N=5)	153	56.5 – 246
Wood Duck (reference, N=6)	57.2	1.1 – 334
Hooded Merganser (Shiawassee, N=4)	288	0.8 – 608
Hooded Merganser (reference, N=3)	11.8	8.5 - 17.0

4.2 Mammalian Piscivores

Toxicity Reference Values - Mink

A number of studies have established that mink (*Mustella vison*) are highly sensitive to PCHs in their diet (e.g., Aulerich *et al*., 1985; Hochstein *et al*., 1988; Heaton *et al*., 1995). These and other studies have established that mink is certainly among the most sensitive mammalian species yet tested, and may be the most sensitive (Tillitt *et al*., 1996).

Three studies have identified critical thresholds for PCHs in mink diet. These and their results are described below:

Hochstein et al. (1988) fed captive mink with diets that were supplemented with seven different concentrations of TCDD (from the control to 100 parts per billion) and measured their reproductive success. At 100 pg/g TCDD in the diet, there were clear impairments in reproduction, with the dosed females mating less successfully, fewer females producing young, and fewer young produced per female. At the next lower dose (10 pg/g in the diet), a smaller percentage of females produced young than the controls, though those that did produced as many young as mink exposed to smaller dietary concentrations of TCDD. Thus, the LOAEC in this study can be determined as being between 10 and 100 pg/g in the diet. Correspondingly (and using a LOAEC – NOAEC uncertainty factor of 10), the NOAEC is between 1 and 10 pg/g TCDD or TCDD-EQ in the diet.

Brunstrom et al. (2001) exposed captive mink to a PCB-contaminated diet. The lowest level of contamination in the diet that resulted in reproductive impairment (reduced kit survival) was 22 pg/g TCDD-EQ. Consequently, using a LOAEC - NOAEC uncertainty factor of 10, the estimated NOAEC is 2.2 pg/g TCDD-EQ in the mink diet.

Giesy et al. (1994b), Heaton et al. (1995), and Tillitt et al. (1996). Heaton *et al. (1995)* found that feeding Saginaw Bay carp to captive mink at as little as 10% of their diet elicited a significant reduction in kit body weights and survival. In a companion paper on the same study, Giesy *et al*. (1994b) using the H4IIE bioassay reported that the lowest contamination level in the mink diet that elicited reproductive impairment (i.e., the 10% carp diet) was 19.4 pg/g wet weight TCDD-EQ. Assuming that this was the LOAEC, and using an uncertainty factor of 10, Giesy *et al*. (1994b) calculated a mink diet NOAEC of 2 pg/g TCDD-EQ, similar to the NOAECs established by Hochstein *et al*. (1988) and Brunstrom *et al.* (2001). Tillitt *et al*. (1996) analyzed the congeners present in the Saginaw Bay carp tissue and, using H4IIE-derived TEFs, reported a total of 194 pg/g TCDD-EQ in the fish; using International TEFs, the corresponding value was126 pg/g. Tillitt *et al*. (1996) also found that the percent contributions of each of the major classes of PCH to the total toxicity in the carp were: PCDFs (55.9%), PCDDs (22.4%), non-ortho-PCBs (20%), and mono-ortho-PCBs (<1%). Thus, in the Saginaw Bay carp that were fed to the mink in this series of studies, PCDFs contributed a majority of the toxicity. Recalculating TCDD-EQ from the Tillitt *et al*. (1996) data, but using WHO mammalian TEFs instead of International TEFs, results in a total TCDD-EQ of 77.8 pg/g in the carp. This calculation assumes a 20% contribution to the total by PCBs (see above). Thus, a 10% diet (approximating 7.8 pg/g) led to reproductive impacts in the mink. Based on this, the NOAEC may approximate 0.8 pg/g.

Other risk-based TRVs. Based on review of the available toxicity literature and food intake modeling, U.S. EPA (1993a) estimated that a fish tissue TCDD concentration of 0.7 pg/g would pose a "low risk" to mammalian wildlife, while a concentration of 7 pg/g would pose a "high risk". U.S. EPA (1993a) does not define what is actually meant by low and high risk. However, at various places in the text it can be reasonably inferred that high risk may involve substantial effects to individuals and/or populations.

Kubiak and Best (1991) in an analysis of risks to Great lakes wildlife from PCHs used a mink dietary NOAEC of 1.9 pg/g TCDD-EQ. This value appears to have been based on the results of the Heaton *et al*. (1995) feeding study.

Kannan *et al*. (2000) reviewed the literature for European otter (*Lutra lutra*) and mink and derived a TCDD-EQ dietary NOAEC for both species of 1 pg/g. In a similar analysis and using data from Tillitt *et al*. (1996), Giesy and Kannan (1998) used a dietary TCDD-EQ TRV of 0.3 pg/g in a risk analysis for mink along the Buffalo River, New York.

The LOAECs and NOAECs from the above sources are summarized in Table 4-10. These data assume that the "low risk" value from U.S.EPA is a NOAEC, whereas the "high risk" value is a LOAEC.

Table 4-10. Summary of dietary TCDD-EQ LOAECs and NOAECs.

LOAEC (pg/g)	**NOAEC (pg/g)**	**Authority**
7	0.7	U.S. EPA, 1993a
10 – 100	1 – 10	Hochstein *et al*., 1988
22	2.2	Brunstrom *et al*., 2001
19.4	2	Giesy *et al*., 1994b
	1.9	Kubiak and Best, 1991
7.8	0.8	From Tillitt *et al*., 1996
2.0	1.0	Kannan *et al*., 2000
	0.3	Giesy and Kannan, 1998

In this ecological risk assessment, we extrapolate from the data in Table 4-10 that a sufficiently protective dietary NOAEC for mink in the study area is 1 pg/g TCDD-EQ in the diet. This is consistent with all of the studies in Table 4-10. This value of 1 pg/g TCDD-EQ is the TRV that is used in Section 5 of this report to estimate risks to mink from consuming contaminated fish from the Tittabawassee River.

Toxicity Reference Values - River Otter

Based on primary studies by Murk *et al*. (1998) and Smit *et al*. (1996), Kannan *et al*. (2000) calculated a dietary NOAEC of 1 pg/g for the European otter. No corresponding data have been found for the river otter. However, this species is closely related in its ecology and taxonomy to the European otter and the mink and in this ERA we have assumed that river otter is as sensitive to PCHs as these species. Thus, the derived river otter NOAEC is 1 pg/g in the diet. This value of 1 pg/g TCDD-EQ is the TRV that is used in Section 5 of this report to estimate risks to river otters from consuming contaminated fish from the Tittabawassee River.

5. RISK CHARACTERIZATION

In this chapter, the TRVs and exposure estimates calculated in Sections 4.1 and 4.2 of this report are combined to estimate risks to avian and mammalian consumers of fish from the Tittabawassee River (Sections 5.1 and 5.2, respectively). Section 5.3 summarizes these risk predictions.

5.1 Avian Piscivores

The estimated avian egg TCDD-EQ from Table 4-8 were translated into Hazard Indices (Table 5-1) using the three TRVs identified in Section 4-1 (also shown in Table 5-1).

Table 5-1. Estimated TCDD-EQ (pg/g, wet weight) in eggs of avian piscivores exposed to PCHs in fish from Tittabawassee River and resulting Hazard Indices (HI). The values in parentheses are the TRVs determined in Section 4.1)

	Carp	**Catfish**	**Shad**	**Bass**	**Mean of All fish**
Egg TCDD-EQ	2223	930	638	333	1031
HI (5 pg/g)	445	186	128	66	206
HI (50 pg/g)	44	19	13	7	21
HI (100 pg/g)	22	9	6	3	10

The results in Table 5-1 indicate that a diet of any of the fish species analyzed will result in HIs greatly exceeding 1 for all of the TRVs. For carp, the most contaminated species, the HIs range from 22 up to 445, while for bass, the cleanest, they range from 3 up to 66. These data indicate that even birds in the Least Sensitive category would be at risk from a diet of any of these fish species (even if the diet was restricted to the least contaminated species). For birds in the Less and Most Sensitive categories and/or that are feeding on more contaminated fish species, the HIs are extremely high and the possibility that such exposure would lead to severe population effects cannot be discounted.

The HI results in Table 5-1 assume that the piscivorous birds are feeding entirely on carp, catfish, shad and/or bass. Even if we assume that this is not the case and that these species make up only a small part of the birds' diets, risk still pertains. For example, if we assume that these four fish species only comprise 10% of the diets of fish-eating birds and that the remainder of the fish eaten from the Tittabawassee River have only half the TCDD-EQ body burdens that the carp, catfish, shad and bass have (515 pg/g), the HIs for the three sensitivity categories would still greatly exceed acceptable levels, at 114, 11, and 5, respectively. Thus, even after adopting unreasonably unprotective assumptions, the risks posed to piscivorous birds from consumption of fish from the Tittabawassee River are still serious.

The above conclusions are supported by data in U.S. EPA (1993a) in which it was determined that fish tissue TCDD concentrations of 60 pg/g or more would pose a "high risk" to sensitive bird species. The actual fish tissue TCDD-EQ concentrations (Table 4-7) exceed this threshold for all four species. This indicates that birds that consumed only the less contaminated species would still be at "high risk".

Table 5-2 shows that the comparative contributions of individual PCH congeners to the total estimated TCDD-EQ in the eggs vary, depending on fish species. In general, 2,3,4,7,8-PeCDF contributes half or more of the TCDD-EQ. In carp, catfish, and bass, 2,3,7,8-TCDF contributes from 4.5 to 12 % of TCDD-EQ, while in shad it contributes over 30%. 2,3,7,8-TCDD also varies across species by a factor of more than 2, being highest in catfish and lowest in carp. Across all fish species, the contribution by individual congeners follows the pattern 2,3,4,7,8-PeCDF> 2,3,7,8-TCDD>2,3,7,8-TCDF>1,2,3,7,8-PeCDD>1,2,3,6,7,8-HxCDD/F.

Table 5-2. Percent contributions by individual PCDD/PCDF congeners to estimated total TCDD-EQ in bird eggs.

Fish Species	**2,3,7,8-TCDD**	**1,2,3,7,8-PeCDD**	**1,2,3,6,7,8-HxCDD**	**2,3,7,8-TCDF**	**2,3,4,7,8-PeCDF**	**1,2,3,6,7,8-HxCDF**
Carp	148	2	<1	4	79	<1
Catfish	29	6	<1	<1	64	<1
Shad	19	2	<1	31	47	<1
Bass	33	3	<1	12	51	<1
All fish	24	3	<1	12	60	<1

5.2 Mammalian Piscivores

To evaluate risks to mink and river otter due to PCH contamination in the Tittabawassee River, concentrations of PCDDs and PCDFs in the tissues of fish collected in 2003 from the Tittabawassee River (Table 5-3) were compared with the mammalian NOAECs established in Section 4.2.

The estimated dietary exposure levels for the 4 fish species collected in 2003 are shown in Table 5-3. These are the mean fish tissue TCDD-EQs obtained using the actual concentrations of each congener and WHO mammalian TEFs. Table 5-3 also shows the percent contributions of the individual congeners to the total TCDD-EQ: across all four species, 2,3,4,7,8-PeCDF generally contributes more than half of the total TCDD-EQ, with 2,3,7,8-TCDD and 2,3,7,8-TCDF contributing more than half of the remainder. Differences are also seen among the fish species: 2,3,7,8-TCDF contributes from only 1% (catfish) to 44% (shad). This is at the expense of 2,3,4,7,8-PeCDF which varies from 34% (shad) to 59% (catfish) and 69% (carp).

Table 5-3. TCDD-EQ (pg/g) in tissues of fish collected by MDEQ in 2003 from the Tittabawassee River. TCDD-EQ calculated using fish tissue congener concentration data in Table 4-7 and WHO mammalian TEFs. Numbers in parentheses are the percent contributions of each congener to the total TCDD-EQ.

	2,3,7,8-TCDD	1,2,3,7,8-PeCDD	2,3,7,8-TCDF	1,2,3,7,8-PeCDF	2,3,4,7,8-PeCDF	1,2,3,4,7,8-HxCDF	1,2,3,6,7,8-HxCDF	1,2,3,7,8,9-HxCDF	Other congeners	Total TCDD-EQ
Carp N=26	10.8 (8)	5.3 (4)	10.1 (8)	3.2 (2)	87.5 (69)	4.8 (4)	1.5 (1)	2.5 (2)	1.9 (1)	128
Catfish N=24	9.4 (18)	5.4 (11)	0.6 (1)	0.04 (<0.1)	29.9 (59)	0.6 (1)	0.2 (<1)	3.3 (6)	1.1 (2)	50
Shad N=23	4.2 (9)	1.5 (3)	19.5 (44)	1.3 (3)	15.2 (34)	0.7 (2)	0.3 (<1)	1.0 (2)	0.6 (1)	44
Bass N=12	3.8 (21)	1.1 (6)	4.0 (22)	0.01 (<0.1)	8.5 (46)	0.3 (2)	0.1 (<1)	0.2 (1)	0.3 (2)	18
Mean of all 4	7.0 (11)	3.3 (5)	8.5 (14)	1.1 (2)	35.2 (59)	1.6 (2.0)	0.5 (<1)	1.7 (3)	1.0 (3)	60

Mink are opportunistic predators and the percentage of fish in their diet may vary. Alexander [(1977), reported in U.S. EPA, 1993b] analyzed the stomach contents of mink from Michigan rivers and streams and found that fish generally comprised 61 to 85% of the wet weight contents. In Table 5-4 Hazard Indices have been calculated assuming that the diet may vary between 10 and 100% carp, catfish, shad, and/or bass from the Tittabawassee River. These values were calculated assuming a TRV of 1 pg/g TCDD-EQ and using the TCDD-EQ data in Table 5-3. The results in Table 5-4 show that even if carp, catfish, shad, and bass comprised only 10% of the mink diet, the HI would still be 6. This calculation assumes, however, that the fish component of mink diet comprises only carp, catfish, bass, and shad, and that the remainder of their diet is entirely uncontaminated with PCHs. Being opportunistic predators, mink are likely to also depredate other species. If we assume that the mink diet comprises only 10% carp, catfish, bass and shad, and that the remainder of their diet has only half the TCDD-EQ body burdens of those 4 species, the HI for mink becomes 33, still greatly exceeding an acceptable level.

Table 5-4. Mink Hazard Indices according to percentage fish from the Tittabawassee River in the diet. Data in parentheses are percent of each species in the diet that would result in an HI of 1 or less.					
% Fish	**Carp**	**Catfish**	**Shad**	**Bass**	**All fish**
100	128	50	44	18	60
90	115	46	40	16	54
80	102	40	35	15	48
70	89	35	30	13	42
60	76	30	27	11	36
50	64	25	22	9	30
40	51	20	18	7	24
30	38	15	13	5	18
20	26	10	9	4	12
10	13	5	4	2	6
	(0.8%)	(1.9%)	(2.2%)	(5.5%)	(1.7%)

In a second stage of this analysis, the maximum percent carp, catfish, shad, and bass in the mink diet that would result in an HI of 1 or less (i.e., a protective dietary level) was calculated from the data in Table 5-4. These percentages are shown in parentheses in Table 5-4. These data show that for mink feeding on these species from the Tittabawassee River, the maximum proportion of fish in the diet could not be higher than 1.7%, if elevated risk was to be avoided. If the mink were preying on one particular fish species, the corresponding numbers would range from 0.8% (carp) to 5.5% (bass). Again, it is important to note that these calculations require that the remainder of the mink diet would be uncontaminated with PCHs. However, unless the mink were obtaining the remainder of their diet from outside the floodplain, this would be very unlikely. In fact, it is much more likely that the total exposure and risk to mink in the river/floodplain system would comprise risk due to consuming both contaminated fish from the river and contaminated terrestrial prey from the floodplain. Thus, the maximum percent values shown in Table 5-4 probably overestimate the amount of fish that a mink could consume without incurring risk.

These conclusions are supported by data from U.S. EPA (1993a) where it was estimated that consumption of fish with tissue concentrations of TCDD that exceed 7 pg/g would result in “high risk” to mammalian wildlife. The least contaminated fish, bass, in Table 5-3 exceeds this threshold by a factor of 2.6, while the other species exceed it by factors of up to 18.

The risk levels estimated in this study are supported by actual empirical data from the study in which carp from Saginaw Bay were fed to captive mink [Giesy *et al*. (1994b), Heaton *et al*. (1995), and Tillitt *et al*. (1996)]. The TCDD-EQ in these carp averaged 77.8 pg/g (WHO mammalian TEFs), which, at a 10% representation in the diet, resulted in a significant impairment of reproductive success in the mink. In the carp collected for this ecological risk assessment in the Tittabawassee River, the average carp TCDD-EQ was 127.6 pg/g, a factor of 1.6 higher than the concentration in the Saginaw Bay carp. This confirms the risks potentially incurred by the consumption of this fish species from the Tittabawassee River and implies that if only 6% of such were fed to captive mink they would suffer significant reproductive impairment.

In another ecological risk assessment performed for mink in the Great Lakes, Giesy *et al*. (1994b) estimated HIs that are very similar to those estimated in this study. For river reaches downstream of dams on the Au Sable, Manistee, and Muskegon Rivers, HIs were 8.9, 21, and 34 (assuming a 100% fish diet). The corresponding value from this study is 60. Giesy *et al*. (1994b) also calculated the maximum allowable percentage of fish in the diet of mink in these rivers if unacceptable risk was to be avoided. This value was 9.9%, which compares with 1.7% in this ecological risk assessment. The fish collected below dams on these three rivers had TCDD-EQ (established using H4IIE assays) of from 12 to 70 pg/g. These compare with the range of 18 to 128 found in this study. Thus, the HIs calculated in this ecological risk assessment and the underlying fish PCH contamination levels are supported by the results of the Giesy *et al*. study (Table 5-5).

Giesy and Kannan (1998) performed an analysis of risks to mink consuming fish from the Buffalo River, NY. Assuming a TRV of 0.3 pg/g, they estimated that 57 pg/g TCDD-EQ in fish tissue would result in a HI of 190 (Table 5-5). If a similar TRV had been used in this ERA, the HI would have been 180.

Table 5-5. Comparison of the results of this study and that of two others. All studies assume a 100% fish diet

	Fish TCDD-EQs (pg/g)	**Hazard Indices**	**Maximum allowable % fish in diet**
Giesy *et al*. (1994b)	12 – 70	8.9 – 34	9.9
Giesy and Kannan (1998)	57	190	
This study	18 – 128	60	1.7

To a smaller extent than mink, river otters are also opportunistic predators. However, fish normally comprise more than 90% of their diet (from data reported in U.S. EPA, 1993b). Assuming a diet that is 100% carp, catfish, shad, and/or bass from the Tittabawassee River and a dietary TRV of 1 pg/g TCDD-EQ in fish tissue (see above), the resulting HIs are presented in Table 5-6.

Table 5-6. Estimated Hazard Indices incurred by river otters with a diet of 100% fish from the Tittabawassee River	
Fish species	**HI**
Carp	128
Catfish	52
Shad	44
Bass	18
All fish	60

The data in Table 5-6 show that river otters on the Tittabawassee River would be exposed to high levels of risk through contamination of their diet by PCDD/PCDFs. Even if the river otters ate only the cleanest fish species (bass) the resulting HI still indicates a high level of risk. The HIs in Table 5-6 also indicate that river otters on the Tittabawassee River would be exposed to higher risk levels than mink. This is because of their greater dependence on a fish diet.

5.3 Summary of Risk Characterization

Avian piscivores

The analysis reported above shows that piscivorous birds consuming carp, catfish, shad, or bass from the Tittabawassee would be exposed to high levels of risk of reproductive impairment. This conclusion applies to species that are sensitive to the effects of PCHs and to relatively insensitive species. Even if the birds ate only the cleaner fish in this analysis, or if the fish in this analysis comprised only a small part of their diet and the remainder was substantially less contaminated, they would still be at risk. These risks are due to high concentrations of PCDFs and PCDDs, with the greatest contributions from 2,3,4,7,8-PeCDF, 2,3,7,8-TCDD, and 2,3,7,8-TCDF.

Mammalian piscivores

This analysis has shown that consumption of carp, catfish, shad, or bass from the Tittabawassee River would expose mink and river otter to high levels of risk of reproductive impairment. Even if the two mammals ate only the cleanest of the four species of fish, high risk levels would still be incurred. Given that river otter are dependent mainly on fish, it is extremely unlikely that a stable population could persist in the face of this risk. Even mink, which may eat organisms other than fish, would have to virtually eliminate fish from their diet to avoid this risk. Even if mink were able to do this, they would have difficulty finding a “clean” source of food to replace the fish, since the adjoining floodplain also is pervasively contaminated with PCHs (MDEQ, 2003).

6. RISK-BASED SEDIMENT CONCENTRATIONS

6.1 Sediment Threshold Concentrations of PCDDs/PCDFs

To provide support to future remediation of the sediments in the Tittabawassee River, and to evaluate the potential risks posed by PCDDs and PCDFs in sediments in Saginaw River and Saginaw Bay, the results of this ERA were used to identify "safe" Sediment Threshold Concentrations (STCs). These are the maximum concentrations of TCDD-EQ in the sediments that should not result in unacceptable HI (i.e., >1) in exposed avian and mammalian piscivores.

The STCs were calculated by dividing the mean TCDD-EQ concentrations in surface sediments of the Tittabawassee River (calculated using WHO avian and mammalian TEFs) with the HIs estimated in Section 5 of this report. This calculation is a simple proportionality: if the sediment TCDD-EQ is x pg/g and results in a HI of y, a HI of 1 would result from a sediment concentration of x/y. The results of these calculations are shown in Table 6-1.

Table 6-1. Calculation of STCs from Tittabawassee River sediment TCDD-EQ and estimated hazard indices for avian and mammalian receptors.

TRV (pg/g)	Mean TCDD-EQ (pg/g, dw) in Tittabawassee River sediments (WHO avian TEFs)	Mean TCDD-EQ (pg/g, dw) in Tittabawassee River sediments (WHO mammalian TEFs)	Hazard Index	Estimated STC (TCDD-EQ pg/g, dw)
Bird egg – 5	2,109		206	10
Bird egg – 50	2,109		21	100
Bird egg- 100	2,109		10	211
Mink		518	45	12
River otter		518	60	9

The STCs for birds range from 10 to 211 pg/g (dw) and for mammals from 9 to 12 pg/g (dw). It should be noted that using TEFs in this way does not imply any potential *direct* toxicity linkage between the sediments and the receptors (since the risk to the receptors is expressed through food chain transfer of contaminants from the sediments to the exposed resources). It does provide a useful accounting tool for identifying sediment TCDD-EQ concentrations of concern.

The STCs estimated in this ERA are compared in Table 6-2 with risk-based TCDD sediment concentrations estimated by U.S. EPA in U.S. EPA (1993b). Although it is not possible to precisely extrapolate the concentration at which risk *begins* to occur from the U.S. EPA thresholds, there is considerable overlap between the two sets of STCs.

Table 6-2. Sediment Threshold Concentrations (pg/g) for avian and mammalian wildlife estimated in this study and from U.S. EPA (1993b).

	EPA "low" risk	EPA "high" risk	Avian STC	Mammalian STC
Avian	21	210	10-211	
Mammalian	2.5	25		9 – 12

6.2 Tittabawassee River

Using the STCs identified in Table 6-1 and Tittabawassee River surface sediment concentrations converted to TCDD-EQ using WHO avian and mammalian TEFs, the TCDD-EQ concentration at each sample site was allocated to one of four STC exceedence categories. These were: less than the STC; between the STC and 10 times the STC; between 10 and 100 times the STC; and greater than 100 times the STC. The results are shown in Figures 6-1 through 6-5.

These data show that the only areas where sediment TCDD-EQ concentrations are lower than the STCs occur upriver of Midland and, immediately downriver of Midland for the two less stringent avian categories. This area downriver of Midland is one in which river flow is comparatively high, deposition is low, and the sediments lack a high organic content (Allan Taylor and Allan Brouillet, MDEQ, *pers comm*). In river sections with these characteristics, PCH concentrations would be expected to be lower than in areas with a higher organic carbon fraction in the sediments.

From these areas downstream the data in Figures 6-1 through 6-5 show little evidence for risk "hotspots", i.e. areas where risk is high and that are surrounded by low risk areas. In fact, the risk appears to be pervasively high throughout the river. No areas of low risk were detected. This could partly be a function of the sampling method which focused on depositional areas and avoided erosional areas. Therefore, lower risk areas might not have been detected. It is possible that if further sampling was to be carried out in erosional areas, hotspots could be delineated.

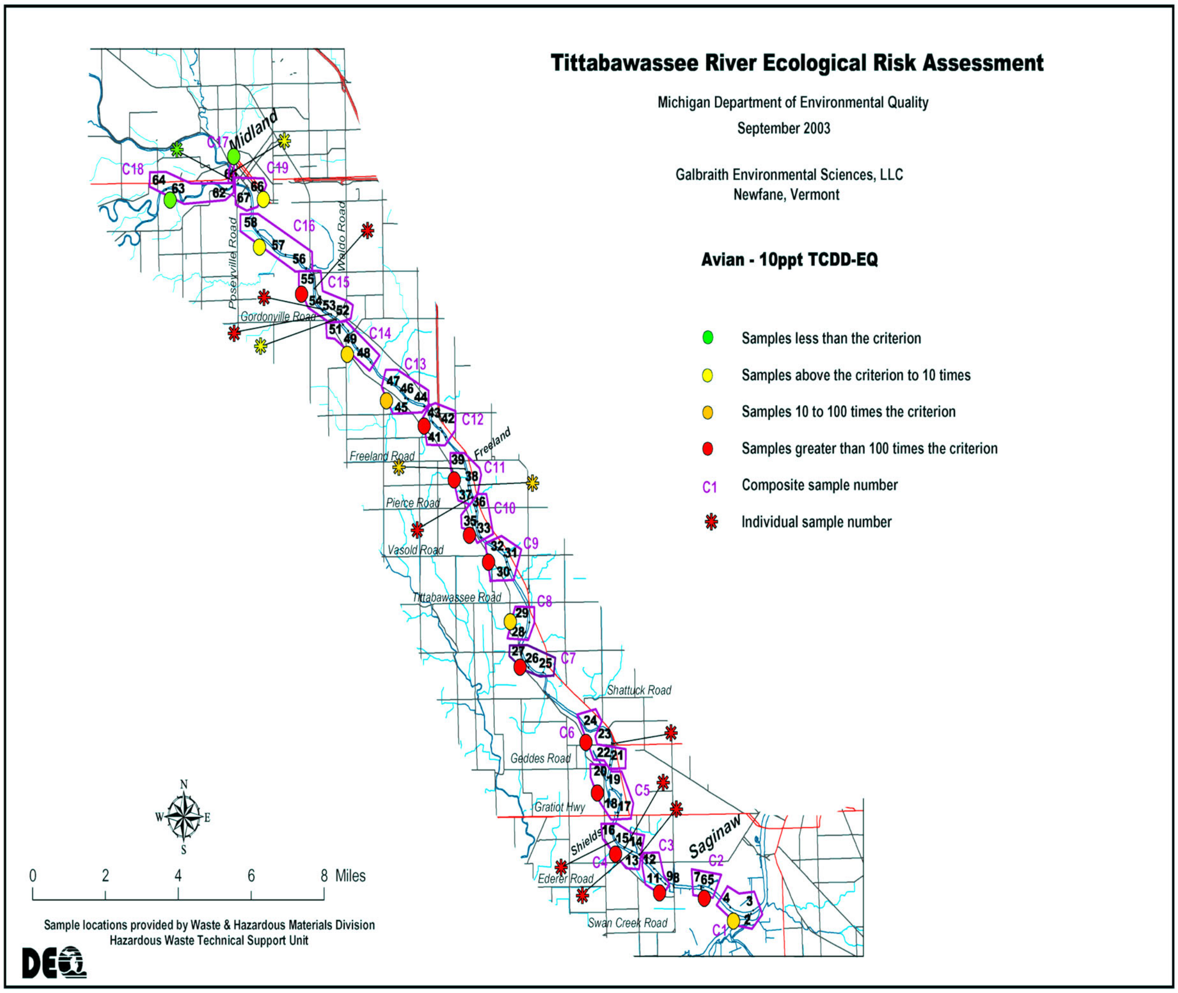


Figure 6-1. Tittabawassee River surface sediment TCDD-EQ concentrations (WHO avian TEFs) relative to the 10 pg/g avian STC criterion.

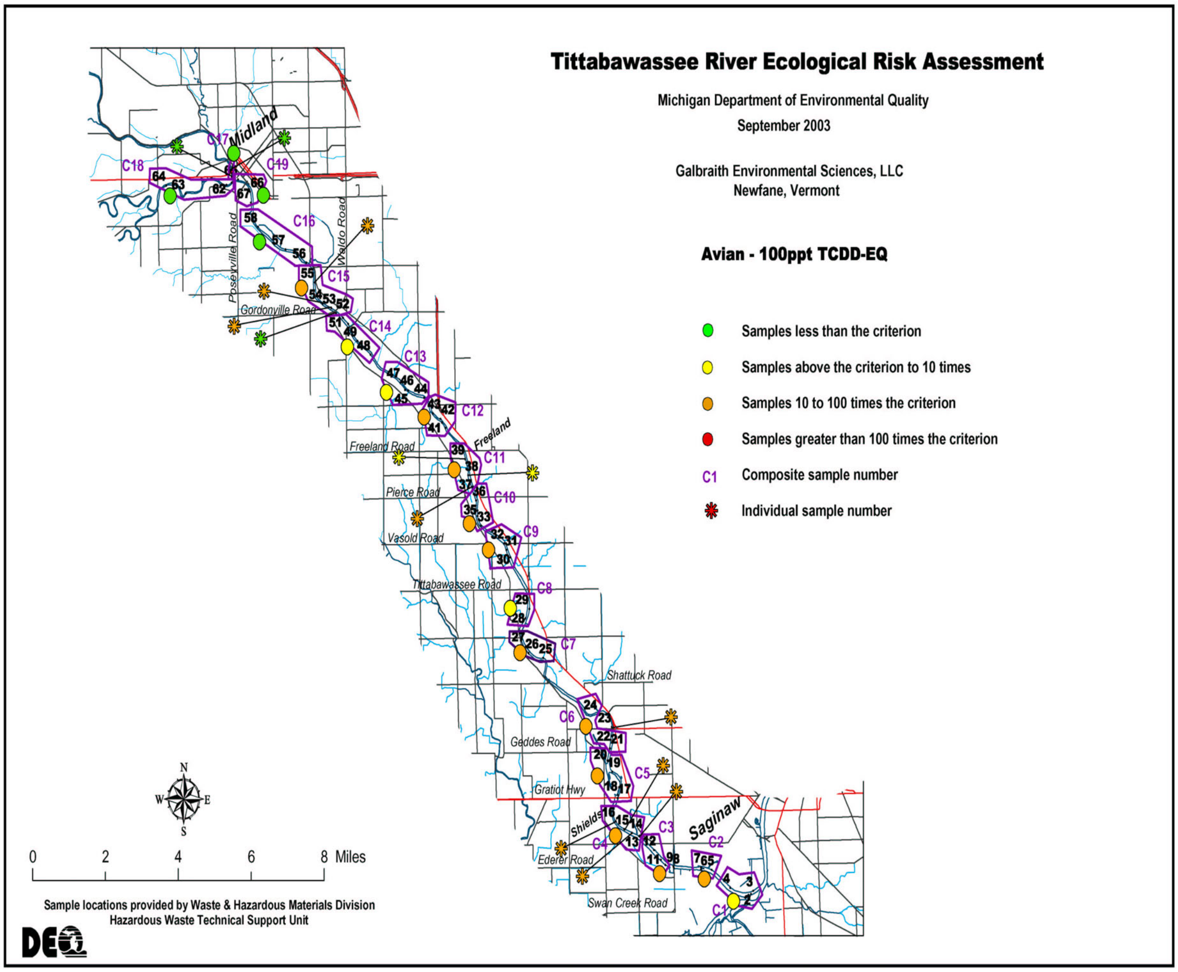


Figure 6-2. Tittabawassee River surface sediment TCDD-EQ concentrations (WHO avian TEFs) relative to the 100 pg/g avian STC criterion.

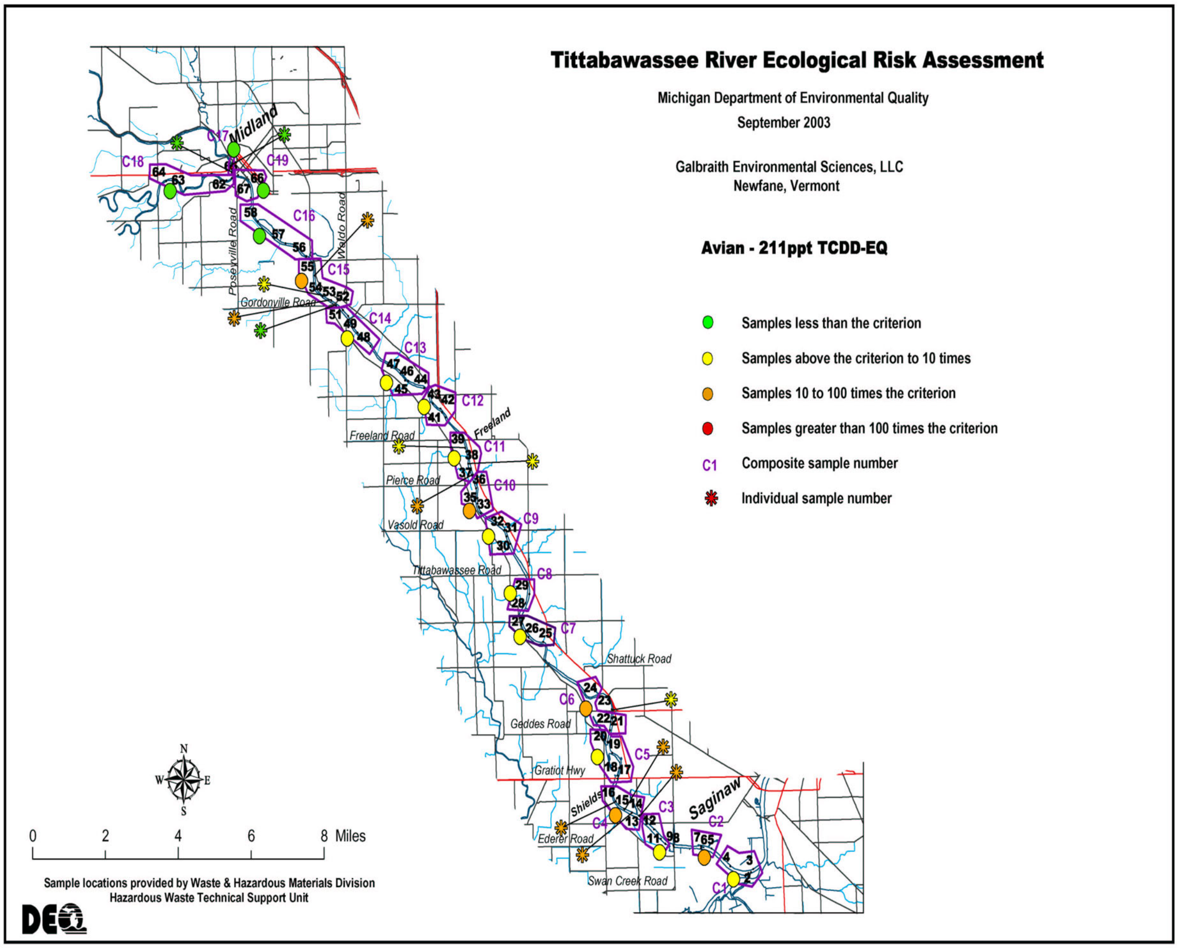


Figure 6-3. Tittabawassee River surface sediment TCDD-EQ concentrations (WHO avian TEFs) relative to the 211 pg/g avian STC criterion.

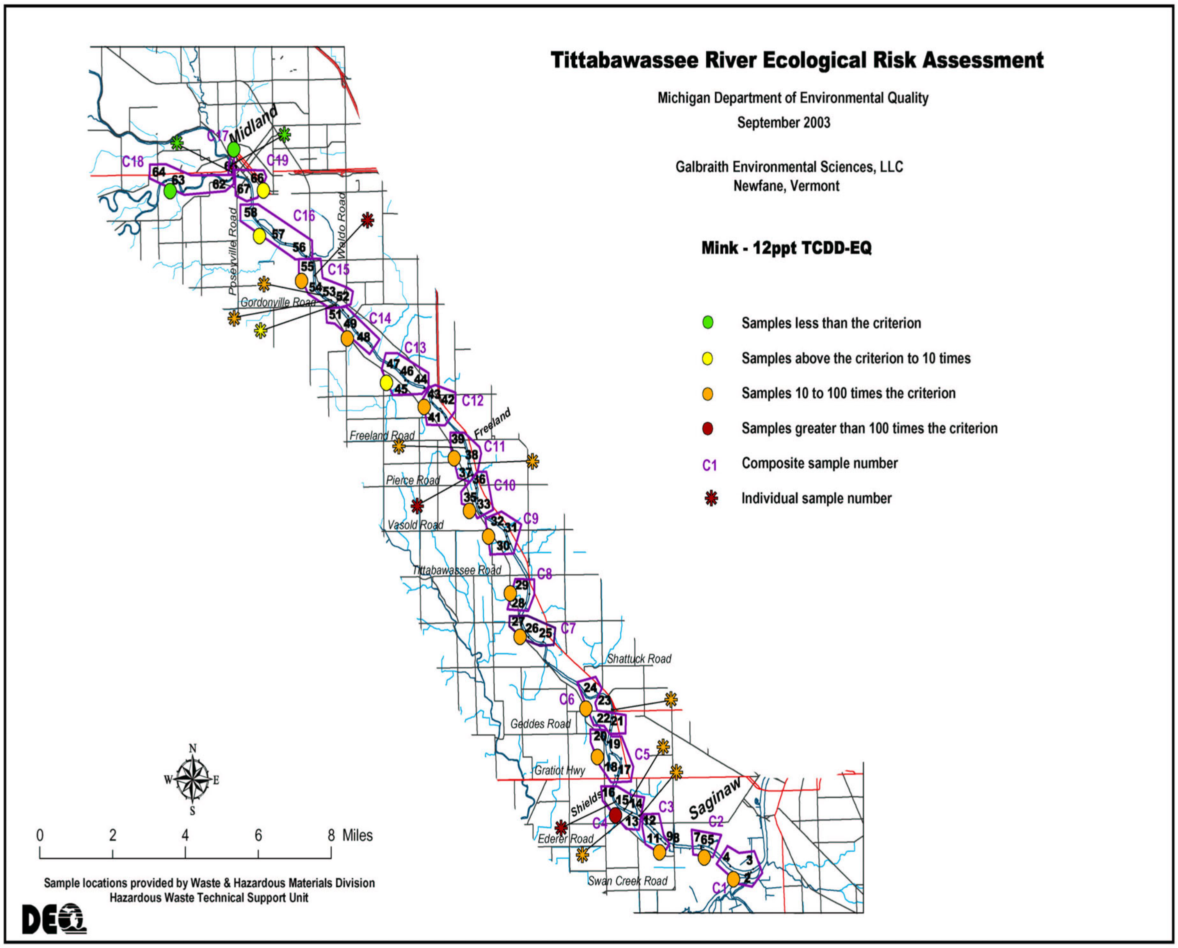


Figure 6-4. Tittabawassee River surface sediment TCDD-EQ concentrations (WHO mammalian TEFs) relative to the 12 pg/g mink STC criterion.

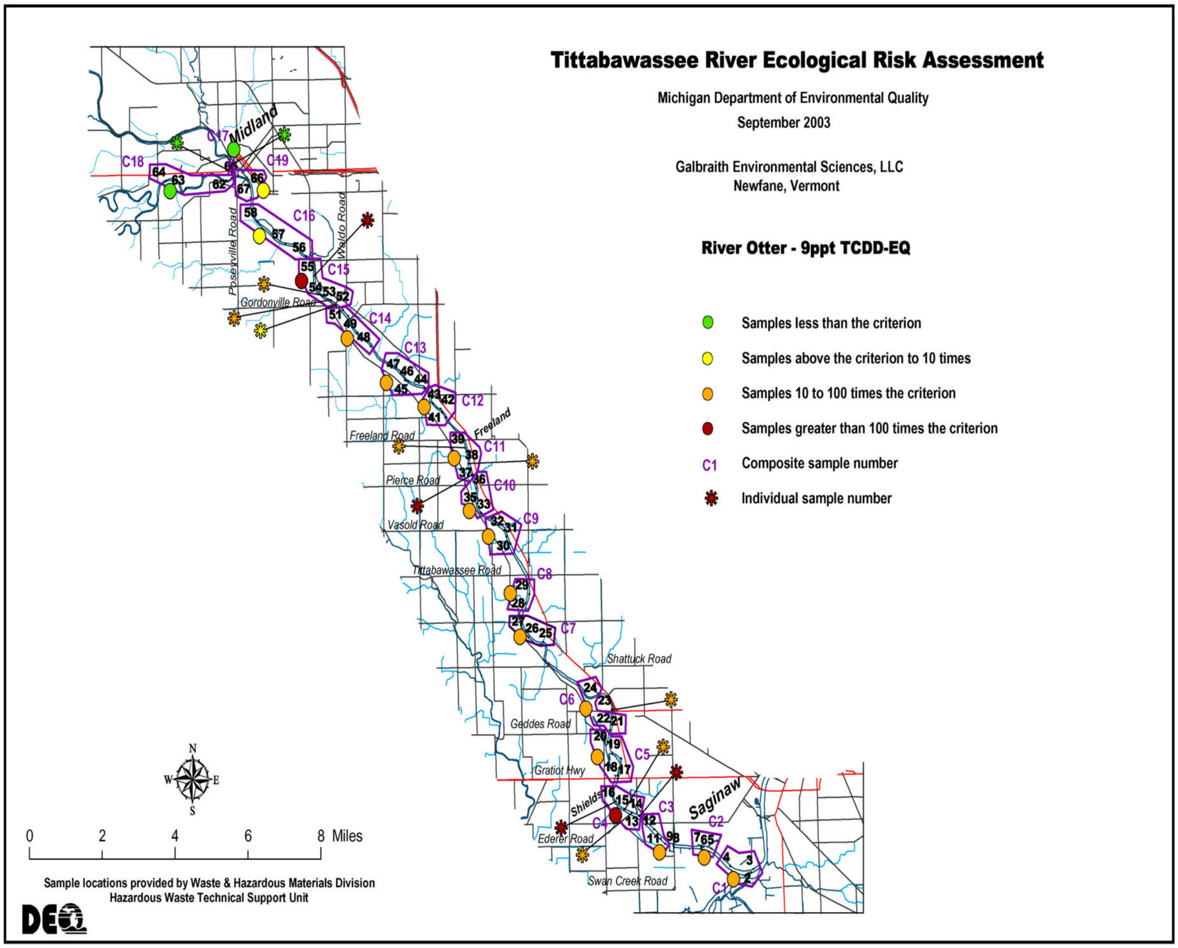


Figure 6-5. Tittabawassee River surface sediment TCDD-EQ concentrations (WHO mammalian TEFs) relative to the 9 pg/g river otter STC criterion.

6.3 Saginaw River and Bay

Table 6-3 shows the results of U.S. Army Corp of Engineers (ACOE) sediment sampling and PCDD/PCDF analyses in Saginaw River and Saginaw Bay in 1998 and 1999 (data supplied by MDEQ and TCDD-EQ calculated using WHO avian TEFs). These data were compared with the avian STCs from Table 6-1. For Saginaw Bay, all 9 samples exceeded the most protective avian STC by factors of up to 61. Eight of the 9 (89%) exceeded the 100 pg/g STC by factors of up to 6, and 5 of the 9 (55%) exceeded the least protective STC by factors of up to 3. For Saginaw River, 25 of the 26 samples (96%) equaled or exceeded the most protective avian STC by factors of up to 217; 21 (81%) exceeded the 100 pg/g STC by factors of up to 22; and 17 samples (65%) exceeded the 211 pg/g STC by factors of up to 10.

Table 6-4 shows the ACOE data converted to sediment TCDD-EQs using the WHO mammalian TEFs. Twenty-two (85%) of the 26 Saginaw River samples exceeded the river otter STC by factors of up to 60. Twenty-one (81%) of the 26 Saginaw River samples exceeded the mink STC by factors of up to 45. All nine Saginaw Bay samples exceeded both mammalian STCs by factors of up to 21.

These comparisons indicate that PCDD and PCDF contamination in Saginaw River and Bay poses risks to avian and mammalian receptors. This conclusion is supported by previous studies: in a feeding study of mink using carp from Saginaw Bay, Tillitt *et al*. (1996) found that the percent contributions of each of the major classes of PCH to the total toxicity in the carp were: PCDFs (55.9%), PCDDs (22.4%), non-ortho-PCBs (20%), and mono-ortho-PCBs (<1%). Thus, in the Saginaw Bay carp that were fed to the mink in this study, PCDFs contributed most of the toxicity and resulted in significant adverse impacts to their reproduction (Heaton *et al*., 1995).

Table 6-3. Total TCDD-EQ (pg/g) from PCDD/PCDF in Saginaw Bay and Saginaw River sediments (calculated using WHO avian TEFS)			
Saginaw River Sample ID	**Total TCDD-EQ**	**Saginaw Bay Sample ID**	**Total TCDD-EQ**
SR9901	227	SB9901	610
SR9902	169	SB9902	565
SR9903	1,293	SB9903	408
SR9904	162	SB9904	335
SR9905	971	SB9905	531
SR9906	311	SB9906	150
SR9907	45	SB9907	79
SR9908	111	SB9908	121
SR9909	334	SB9909	109
SR9910	365		
SR9911	2,176		
SR9912	494		
SR9913	9		
SR9914	31		
SR9915	10		
SR9916	116		
SR9917	776		
SR9918	471		
SR9919	308		
SR9920	334		
SR9921	508		
SR9922	32		
SR9923	314		
SR9924	731		
SR9925	426		
SR9926	486		

Table 6-4. Total TCDD-EQ (pg/g) from PCDD/PCDF in Saginaw Bay and Saginaw River sediments (calculated using WHO mammalian TEFS)			
Saginaw River Sample ID	**Total TCDD-EQ**	**Saginaw Bay Sample ID**	**Total TCDD-EQ**
SR9901	83	SB9901	188
SR9902	45	SB9902	187
SR9903	342	SB9903	130
SR9904	42	SB9904	107
SR9905	331	SB9905	176
SR9906	66	SB9906	55
SR9907	11	SB9907	28
SR9908	25	SB9908	48
SR9909	91	SB9909	42
SR9910	102		
SR9911	538		
SR9912	171		
SR9913	3		
SR9914	8		
SR9915	3		
SR9916	30		
SR9917	202		
SR9918	109		
SR9919	126		
SR9920	113		
SR9921	143		
SR9922	9		
SR9923	107		
SR9924	255		
SR9925	126		
SR9926	147		

7. UNCERTAINTIES

Uncertainty is an intrinsic part of all ecological risk assessments, and indeed of all studies of the effects of stressors on organisms living under uncontrolled circumstances. Even if highly detailed field studies are performed to provide site-specific data, uncertainty cannot be avoided. Indeed, while reducing some of the original sources of uncertainty, such studies may introduce other sources of uncertainty.

Uncertainty in ERA may arise from a large number of sources but most often because it is usually not possible to accurately predict exposure to all of the potential receptors, or that the stressor response information is not complete and assumptions must be made, or that no stressor-response information exists for the receptor and a surrogate species must be used. Regardless of its source or type, the ERA must, to the extent possible, explicitly recognize and accommodate this uncertainty. If, given the constraints of data availability, it is not possible to entirely eliminate sources of uncertainty, the remaining sources must be brought to the attention of the risk manager.

In this ERA, uncertainty potentially arises from a number of the parameters used. These are identified below and their likely impacts on the certainty with which the risk results can be viewed are discussed.

7.1 Diets of Piscivorous Birds and Mammals in the Assessment Area

No information was found on the diets of the avian or mammalian piscivores in the assessment area. However, the piscivorous species that could be present along the Tittabawassee River (e.g., bald eagles, great blue heron, mink, etc.) are typically opportunistic in their prey selection, taking advantage of whatever fish food sources are most plentiful and easiest to capture (U.S. EPA, 1993b). For this study a total of 85 individual fish of four species were sampled from the Tittabawassee River. Each species is common within the study area and could be assumed likely to feature in the diets of the receptors. Thus, the fish data on which the risk evaluation was based are believed to provide a not unreasonable approximation of the actual exposures of piscivorous receptors in the assessment area.

The HI calculations for the piscivorous birds began by assuming that their diets comprised 100% carp, catfish, bass and shad. This resulted in the high HIs reported in Table 5-1. An indication of the robustness of the conclusion of high levels of risk is given by a subsequent calculation (reported in Section 5-1) that assumed that these 4 fish species comprised only 10% of the birds' diets and that the remaining fish prey had only half the body burdens that carp, catfish, shad, and bass had. Both of these assumptions are unreasonably unprotective. Nevertheless, even with such assumptions, the HIs for the three avian sensitivity categories still greatly exceeded 1, at 114, 11 and 5. A similar calculation for mink (reported in Table 5-4) shows that even if carp, catfish, shad and bass comprised only 2% of the diet, the mink HIs would still exceed 1. In this calculation it was assumed that the remaining 98% of the diet was entirely free from dioxins and furans. This would be impossible in the pervasively contaminated Tittabawassee River floodplain. If we, alternatively, assume that the mink diet comprises only 10% carp, catfish, bass and shad, and that the remainder of their diet has only half the TCDD-EQ body burdens of those 4 species, the HI for mink becomes 33, still greatly exceeding an acceptable level. The 10% and 50% assumptions used in these calculations are unreasonably unprotective, however, they do serve to demonstrate that the conclusion of risk to piscivores in the Tittabawassee River is robust.

This conclusion is also supported by the high concentrations of PCDDs and PCDFs reported in the eggs of hooded mergansers and wood ducks from the Shiawassee NWR, indicating that these species, at least, are exposed to diets that are substantially contaminated by these PCHs.

While we are confident that the fish data do provide a good approximation of exposure to the piscivorous predators, if uncertainty was to be reduced further it could be through sampling additional potential aquatic prey of piscivores in the assessment area. Nevertheless, even if additional fish species were collected and found to be less contaminated than the four species included in this ERA, this would not imply that the risks posed by consumption of those four species would be any lower.

7.2 Avian and Mammalian TRVs

A large data set exists in the peer-reviewed scientific literature describing the sensitivity of bird and mammals species to PCHs. Most of these data apply to PCDD and PCB sensitivity and relatively few to PCDFs. However, using the TEQ approach allows the PCDD and PCB data to be utilized in establishing thresholds for PCDFs. Such TCDD-EQ thresholds have been established in a number of previous ERA for piscivorous wildlife in the Great Lakes Region (e.g., Giesy *et al.*, 1994b and 1994c). For this ERA, this body of knowledge was reviewed and representative TRVs identified. These TRVs are comparable, to a great extent, to those used in previous Great Lakes risk evaluations and guidance published by the U.S. EPA. In addition, for the piscivorous birds the uncertainty surrounding differing sensitivities among species to TCDD-EQ was addressed by establishing three TRV categories, reflecting the differing sensitivities among birds reported in the literature. Thus, the bird TRVs are not biased toward the most sensitive species, but reflect the range observed in nature. Also, given the high HI values estimated in this ERA, the avian TRVs would have to be adjusted by unreasonable amounts to reduce risk estimates to acceptable levels.

It should also be noted that the sensitivities to PCDDs and PCDFs of the vast majority of bird species that occur in the assessment area are unknown. Compared with the numbers of species that occur in the wild, relatively few species have been rigorously tested in the laboratory. Given this uncertainty and the need to avoid false negative results, it should not be assumed that all wild species are somehow less sensitive than the chicken, the most sensitive species thus far tested, (the process of domestication is unlikely to have somehow bred an intolerance to PCHs); in fact, equally or more sensitive species could occur in the wild.

For the piscivorous mammals, uncertainty associated with the TRVs could not be evaluated directly. However, uncertainty is relatively low since laboratory data are available for the actual species of interest. Also, uncertainty was addressed indirectly by estimating the proportion of the diet that would correspond to a “safe” level. This showed that even extremely small fractions of contaminated fish in the diet, as low as a few percent of the total diet, could result in unacceptable levels of risk, and suggests that the

TRVs selected would have to be adjusted by an unreasonable amount to reduce risk estimates to acceptable levels.

7.3 Fish – Bird Egg BMFs

In comparison to TRVs, relatively few studies of diet to bird egg BMFs have been reported in the scientific literature. Consequently, a greater degree of uncertainty is associated with their selection for ERA. Nevertheless, enough studies do exist to allow such a selection for the congeners that contribute most of the risk in the assessment area.

For this study we used a BMF value of 29 for 2,3,7,8-TCDD; the range of BMFs in the literature extends from 19 to 98. We selected the mean of the published studies. This value is closer to the low end of the published range and there is a risk that it may not be protective enough of piscivorous wildlife. However, without site specific data we cannot be certain.

A BMF value of 1 was used for 2,3,7,8-TCDF. Previous studies have asserted (based on limited evidence) that 2,3,7,8-TCDF may not be accumulated high in food chains. However, data from fish, duck, and chicken eggs from the assessment area indicate that it is bioaccumulated in vertebrates. For this reason we have conservatively assumed a BMF of 1. This value is subject to some uncertainty and may not be protective enough.

The published range of BMFs for 2,3,4,7,8-PeCDF extends between 4.5 and 64.6. This study assumes a value of 10, closer to the low end of the published range. This value may not be protective enough, however, too few studies exist to allow a more precise estimate.

Only one BMF value for 1,2,3,7,8-PeDF has been published in the scientific literature. We have used this value (9.7) in this ERA.

It is possible, due to the cautious approach used in the selection of BMFs for this ERA that the actual bioaccumulation in bird eggs of PCDDs and PCDFs in the study area may have been underestimated. The fact that with only 4 samples the maximum hooded merganser egg concentration exceeded 600 (a concentration known to be injurious to many bird species) suggests that this may be so. Without additional data, however, this cannot be confirmed. Nevertheless, it should be borne in mind when interpreting the risk values.

7.4 Sediment Threshold Concentrations

The STCs were estimated in this ERA using the mean sediment TCDD-EQ concentration from data collected by MDEQ in 2001. However, since this sampling effort focused on what were thought to be depositional areas and avoided erosional areas, it may overestimate the actual mean concentration (since erosional areas are likely to have lower organic carbon fractions and PCH concentrations). The result of this is that the STCs calculated in Section 6 of this report may not be protective enough.

7.5 Saginaw River and Saginaw Bay

In comparison to the Tittabawassee River, relatively few sediment PCDD and PCDF congener concentrations exist for the Saginaw River and Saginaw Bay (26 and 9, respectively). Also, the Saginaw Bay sediment samples were collected in a relatively restricted area of the inner bay and none were collected from further out. For this reason, there is some uncertainty regarding the degree and spatial extent of PCDD/PCDF contamination and, therefore, risk to ecological receptors in these two waterbodies. Only further and more detailed sediment sampling could reduce this uncertainty.

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